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THE

CHEMICAL NEWS

AND

JOURNAL OF PHYSICAL SCIENCE.

WITH WHICH IS INCORPORATED THE "CHEMICAL GAZETTE."

A Journal of Practical Chemistry

IN ALL ITS APPLICATIONS TO

PHARMACY, ARTS, AND MANUFACTURES.

EDITED BY

SIR WILLIAM CROOKES, F.R.S., &c.

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THE CHEMICAL NEWS.

VOLUME LXXIX.

EDITED BY SIR WILLIAM CROOKES, F.R.S., &c.

No. 2041.—JANUARY 6, 1899.

RADIUM: A NEW BODY, STRONGLY RADIO-ACTIVE, CONTAINED IN PITCHBLENDE.

By M. P. CURIE, Mdme. P. CURIE, and M. G. BÉMONT.

Two of us have shown that, by purely chemical processes, a strongly radio-active substance can be extracted from pitchblende. This substance is near bismuth in its analytical properties. We therefore came to the conclusion that pitchblende might contain a new element, for which we proposed the name of Polonium (*Comptes Rendus*, vol. cxxvii., p. 175; CHEMICAL NEWS, vol. lxxviii., p. 49).

Our subsequent researches are in accord with the results first obtained, but concurrently with these we have met with a second substance, strongly radio-active, and entirely differing from the first body in its chemical properties.

Polonium is precipitated from its solution by sulphuretted hydrogen. Its salts are soluble in acids, and are precipitated by water; polonium is completely precipitated by ammonia. The new radio-active substance we have discovered has, to all appearance, the properties of almost pure barium. It is not precipitated either by sulphuretted hydrogen nor by ammonium sulphide, nor by ammonia; its sulphate is insoluble in water and acids; the carbonate is insoluble in water; the chloride is very soluble in water, but insoluble in concentrated hydrochloric acid and in alcohol. It gives the barium spectrum easy to recognise. Nevertheless we believe this substance, although in greater part consisting of barium, contains besides a new element which gives to it radio-activity, and which is close to barium in its chemical properties.

Here are the reasons which lead us to this opinion:—

1. Barium and its compounds are not radio-active; also one of us has shown that radio-activity appears to be an atomic property, persisting through all the chemical and physical states of the substance. From this point of view the radio-activity of our substance, not being due to barium, should be attributed to another element.

2. The first substances we obtained had, in the state of hydrated chloride, an activity sixty times as great as that of metallic uranium (the radio-activity was measured by the amount of conductivity conferred on air in our apparatus). On dissolving these chlorides in water and precipitating a portion by alcohol, the part precipitated is much more active than the part left in solution. Taking advantage of this fact we may, by a series of fractionations, obtain chlorides more and more active. We have thus obtained chlorides having an activity 900 times greater than that of uranium. We were stopped here by failure of material, but from the progress of the operations we could see that the activity would have augmented still more had we been able to continue. These facts may be explained by the presence of a radio-active element, the chloride of which is less soluble in alcoholised water than is that of barium.

3. M. Demarçay has been good enough to examine the spectrum of our substance. The results are given in a note following this. M. Demarçay has found in its spectrum a ray which does not appear to be due to any known element. This ray, scarcely visible with the chloride sixty times more active than uranium, is notable with the chloride concentrated by fractionation to an activity 900 times that of uranium. The intensity of this ray augments, therefore, with the radio-activity, and this we think is a very serious reason for attributing it to the radio-active portion of our substance.

These different reasons lead us to believe that the new radio-active substance contains a new element, to which we propose to give the name of radium.

We have determined the atomic weight of our active barium by estimating the chlorine in the anhydrous chloride. We have found numbers differing very little from those obtained with inactive barium chloride; however, the numbers for the active barium are always a little higher, but the difference is of the order of magnitude of experimental errors. The new substance certainly contains a very large proportion of barium; in spite of this its radio-activity is considerable. The radio-activity of radium ought therefore to be enormous.

Uranium, thorium, polonium, and radium, and their compounds, render air a conductor of electricity, and act photographically on sensitive plates. From these points of view polonium and radium are considerably more active than uranium and thorium. On photographic plates we obtain good impressions with radium and polonium in half a minute; it requires several hours to obtain the same result with uranium and thorium.

The rays emitted by compounds of polonium and radium render barium platinocyanide fluorescent; their action in this respect is analogous to that of the Röntgen rays, but is considerably more feeble. To make the experiment place on the active substance a very thin sheet of aluminium, and on this a thin layer of barium platinocyanide; in the dark the barium platinocyanide appears feebly luminous over the active substance.

We thus realise a source of light, very faint, it is true, but functioning without a source of energy. There is here a contradiction, at least apparent, to the principle of Carnot.

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Uranium and thorium under the same circumstances give no light, their action probably being too feeble. —*Comptes Rendus*, vol. cxxvii., p. 1215, Dec. 26, 1898.

ON THE

ANALYSIS OF MOLYBDENUM COMPOUNDS.

By HARRY BREARLEY.

(Continued from vol. lxxviii., p. 205).

II. Separations from Molybdenum.

In this Section we propose to take some elements whose presence interferes with the estimation of molybdenum as lead molybdate when carried out in the ordinary way, although, as will be seen later, it is not always necessary to previously separate such elements.

The adoption of a reagent for separatory purposes obliges us to establish, first, that such reagent itself does not interfere with the estimation of molybdenum, and, secondly, the separation effected by it is at least reasonably accurate. The first consideration at once vetoes a number of processes which admirably answer to the requirements of the second. The obviation of this difficulty, by in turn separating the excess of the first reagent by a less objectionable one, has been disregarded on the ground that such a complication of processes would make the estimation of molybdenum as lead molybdate inferior to its estimation by other means.

Sulphuric Acid.

From the fact that molybdenum occurs in Nature very largely as a sulphide (molybdenite) the interference of sulphuric acid is an important one; it is important also from the fact that as a reagent it forms a number of insoluble sulphates. The estimation of molybdenum in its presence would be falsified by a simultaneous formation of sulphate and molybdate of lead. Theoretically, a resort to ammonium acetate, in which lead sulphate is soluble, should remedy the error, and experiment shows that practicable amounts of acetate can retain very considerable amounts of lead sulphate in solution when no other metal is being precipitated.

Where a separation depends on the presence of a subsidiary reagent whose object it is to prevent the co-precipitation of an objectionable compound, then the *order* in which the operations are performed is frequently a matter of some moment. Thus in the case before us we may avail ourselves of the qualities of ammonium acetate by adding it to the mixture of molybdic and sulphuric acids, or by adding it to the lead acetate, and then, for either way, we may pour into the mixed acids or into the lead acetate. In all, then, there are four ways in which the precipitation of the lead molybdate may be performed, and three of them invariably have given high results. The fourth way has always given very accurate results, and its order is as follows:—Heat to boiling the solution of molybdic and sulphuric acids (part of the H_2SO_4 may be present as free acid), and to an amount of lead acetate more than sufficient to precipitate the molybdenum add, say, 30 c.c. of strong ammonium acetate; heat this also, and then pour *the second mixture into the first;* bring the whole to boiling, filter, &c.

Some results are—

	50 c.c. normal H_2SO_4 present.
20	
0·1000	0·1001
0·0998	0·1000
0·1000	
0·1001	

The precipitates were tested, in each case, for sulphuric acid, with negative results.

Barium, Strontium, and Calcium.

Having established a procedure under which sulphuric acid is innoxious, it remains to enquire whether the precipitation of barium, calcium, and strontium, as sulphates, is an accurate means of separating these elements from molybdenum.

Barium readily forms a molybdate in a neutral or even a slightly acidified (acetic) solution. Indeed the precipitation from neutral or slightly ammoniacal solutions is quantitatively exact for pure molybdates at any rate. To prevent this reaction complicating the precipitation of the barium sulphate, a small quantity of hydrochloric acid—in which $BaMoO_4$ is easily soluble—is added, and then with an excess of sulphuric acid, not needlessly large, the barium is precipitated from a boiling solution.

After ignition the barium sulphate is never perfectly white; it has, particularly when cold, a slight green tinge. If the precipitated $BaSO_4$ be kept boiling for ten or twenty minutes, the tinge is somewhat fainter. If it is caused by associated molybdenum the amount present must, even in the worst cases, have been practically negligible. On purifying the ignited $BaSO_4$, by re-dissolving in strong sulphuric acid and subsequently diluting, the green tinge is always observable in the moist precipitate; but after ignition the precipitate is perfectly white, and its weight hardly differs from the first.

The molybdenum in the filtrate is estimated with the afore-mentioned precautions respecting H_2SO_4.

Test Analyses.

0·1	0·2 grm. Ba present.
0·1001	0·1005 Mo recovered.

Calcium and Strontium.

These two elements are not so completely precipitated as insoluble sulphates as is barium. Happily, however, there are circumstances under which they need not be removed at all, and consequently no trouble was taken to use the various accessories—alcohol, &c.—of a complete precipitation.

Both calcium and strontium form molybdates in neutral solutions. These molybdates are less and less readily formed as the amount of free acetic acid in the solution is increased. Their behaviour in this respect is in the Ba, Sr, Ca order, barium being decidedly the most refractory. When solutions of 200 c.c. contain one or two tenths of a grm. of Ba, Ca, and Sr, along with about 20 c.c. of acetic acid, the molybdates can be formed, even on long-continued boiling, only with barium. On this property of the alkaline earths is based a method of estimating molybdenum in their presence.

Here, as in the presence of sulphuric acid, it is important to add the reagents in a certain order. If to the faintly acid (HCl) solution of molybdenum and strontium (say) there be added ammonium acetate, acetic acid, and lead acetate, in the order stated, the results are invariably 2 or 3 per cent too low, presumably on account of an admixture of the less weighty molybdates of Sr. By dissolving the ignited precipitate in hydrochloric acid, and re-precipitating under like conditions, the error is amended.

The much more accurate way is to add a few c.c. of HCl in excess, then acetic acid and lead acetate. Unless too much HCl has been added, the molybdenum is partially precipitated at this stage; the addition of ammonium acetate completes it. Up to the addition of lead acetate the solution should have been kept at boiling-point; after adding the ammonium acetate the filtration may be proceeded with without further heating. For the sake of brevity I shall subsequently refer to this as the "acid precipitation."*

* The precipitated lead molybdate has at no time been very difficult to filter, but with the acid precipitation it comes down almost sand-like. The filtration of a single sample through paper-pulp is as much as one can comfortably attend to.

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Test Analyses.

	0·1	0·2 grm. added element.
Strontium	0·1001	0·1000
Calcium	0·0997	0·0997

In the application of this procedure to barium it is particularly necessary to avoid boiling after the precipitation is complete, and even so with the same amount of reagents as were used for calcium and strontium the results were from 1 to 2 per cent too low with one precipitation. This is less to be regretted since barium is so completely separated with sulphuric acid.

Extended Application of the Acid Preparation.

I now found that a number of elements which on preliminary trial had been passed over, as needing to be separated, could easily be disposed of by the acid precipitation, and I am of opinion that if this form of precipitation along with pump filters had been adopted for those elements previously tabulated (CHEM. NEWS, lxxviii, 203) there would have been no cause to call attention to the contamination of the lead molybdate with traces even of cobalt, manganese, or nickel.

The test analyses of a number of further elements treated in this way are collected in—

TABLE II.

Metal added.	0·1	0·2 grm. added.
Arsenic	0·0999	0·1001
Cadmium.. ..	0·1000	0·1000
Aluminium ..	0·1003	0·0999
Uranium	—	0·1002

The arsenic, used as potassium arsenite, forms a precipitate with the lead salt even in acetic solutions. This precipitate is not formed if the solution be moderately acidified with nitric or hydrochloric acid, and then the other reagents added in the previously named order.

Uranium was included in Table I. The results of the ordinary precipitation were, however, admittedly unsatisfactory even after re-precipitation. The acid titration furnishes much better results, and, should a re-precipitation be deemed necessary, a more effective way is to dissolve the ignited precipitate in a small excess of soda hydrate in the manner explained below (see Chromium).

Soda Silicate.

As a number of molybdenum compounds can be most readily decomposed by alkaline fusion, silicate of soda frequently obtrudes itself on the analyst's notice. If present in very large amounts the acid solution gelatinises it, and renders any practicable filtration of the lead molybdate impossible. After dehydrating the silica by evaporating the acid (HCl) solution to dryness and baking, the molybdenum is completely re-dissolved by boiling with dilute hydrochloric acid, and is thus separated.

The evaporation is frequently a very slow process. We find it more expeditious and quite practicable with amounts up to half a grm. silica to acidify the solution with HCl and boil. In this way some silica may be precipitated, but it is usually in such a state as does not retard the filtration. After boiling for several minutes the precipitation is completed as usual. It might be thought that simply to re-dissolve the ignited precipitate, and filter off any silica which may have been precipitated, would enable one to correct the result; but such is not the case. It is necessary to re-precipitate the solution after filtering. The following test analyses show results calculated—I. before separating silica, II. after deducting silica, and III. after re-precipitation.

I.	II.	III.	SiO_2 (present as potass. silicate.
0·1015	0·1010	0·1001	0·1 grm.
0·1014	0·1008	0·1002	0·2 ,,
0·1033	0·1007	0·1000	0·3 ,,

Iron.

It is the combinations of iron and molybdenum which most frequently come to my notice, and great pains were therefore taken to precipitate the molybdenum without a preliminary separation of the iron. So far all attempts have been unsuccessful. The compound which molybdenum forms with iron in neutral and nearly neutral solutions is not to be lightly disposed of. It behaves very persistently like the basic chromate of iron, which has been previously shown (CHEMICAL NEWS, lxxvii., p. 49) to falsify a great many analytical schemes.

As the iron had to be separated, a mixture of the two metals was prepared and its free acid determined. Equal amounts of this mixture, containing 0·1 grm. of molybdenum and 0·2 grm. of iron, were precipitated with varying excesses of alkali of two normal strength and raised to boiling. The figures given are the amounts of molybdenum recovered from the filtrate:—

TABLE III.

Alkali used	0	10	30	50 c.c. excess used.
Ammonia hydrate	0·0329	0·0732	0·0849	0·0890
Soda carbonate..	—	0·0936	0·0997	0·0998
Soda hydrate ..	—	0·1000	0·1002	0·1003

The precipitation of iron as basic acetate is perfectly useless as a means of separating iron and molybdenum. The recovery increases with the acetate, but 50 c.c. strong ammonia acetate added to a portion of the solution just used separated only 30 per cent of the molybdenum, and it is possible to arrange a separation so that hardly any molybdenum shall be separated at all. This point is worthy of remark, as there are occasions when it is desirable to have the iron and molybdenum precipitated together. It seems also very probable that alkaline molybdates could be very successfully used like the corresponding chromates (CHEMICAL NEWS, lxxviii., 14), for replacing the acetates in the separation of iron from other members of its own group.

As this process applied to the details of the analysis of steel and steel-making alloys would too greatly interfere with the consideration of other separations, the subject is being treated in a separate paper.

Chromium.

So far as available references go, I find that the customary way of separating molybdenum and chromium is to precipitate the latter element with ammonia. De Benneville, who applies this procedure to the analysis of some molybdenum chromium irons (*Jour. Iron and Steel Inst.*, 1895, 205 and 229), finds that it is necessary to re-dissolve and re-precipitate the chromic hydrate, and also to boil for at least half an hour after adding the ammonia. The former precaution I can quite confirm, and even after that it is easy to imagine that the separation is not perfect, or approximately so. The need for the latter precaution I have not experienced. There is always, of course, the need to boil for a little while so as to re-precipitate the dissolved chromic hydrate, even when solutions of pure chromic salts are being dealt with, but that the precipitation in presence of molybdenum constitutes a special case, and may go astray through the formation of $Cr_2(Mo_2O_7)_33(NH_4)_2Mo_2O_720H_2O$ compounds seems to rest on somewhat slender evidence. However, the point is not an important one since the separation, however performed, is very unsatisfactory. The following test analyses show the effect of using increasing amounts of ammonia:—

5 c.c.	20 c.c.	30 c.c. 2N.NH_4HO in excess.
0·0591	0·0715	0·0785 Mo recovered.

A separation with as little as 10 c.c. of 2N soda hydrate in excess seems to be a very approximately accurate one. If the soda hydrate is added to the cold solution the chromic hydroxide is re-dissolved, but re-precipitated on boiling. If added to the boiling solution the precipitation

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takes place at once, but is never, in either case, *quite* complete, however long the solution be boiled. A little of the chromium, more so if precipitated from cold solutions than otherwise, is always converted into sodium chromate, and is wholly precipitated along with the molybdenum as lead chromate, the condition of precipitation being equally favourable to either acid. This unfortunate interference decreases with the excess of soda used, but as the excess must always exceed a minimum, the error cannot be altogether eliminated if the amount of chromium to be separated is at all considerable.

The most satisfactory procedure is as follows. Nearly neutralise the acid solution of molybdenum and chromium, heat to boiling, and then add an excess of soda hydrate; or if the chromium present is several times larger in amount than the molybdenum, add the mixture to the soda with constant shaking. Boil for about ten minutes, filter off an aliquot portion, acidify, and precipitate the Mo. Both the moist and the ignited $PbMoO_4$ may have a yellow or even an orange colour. Re-dissolve in HCl, add dilute soda hydrate to the heated solution until the precipitate, once formed, just re-dissolves, boil, filter, wash, and from filtrate re-precipitate the lead molybdate after adding a little more lead acetate. The latter precipitate should be only faintly tinted yellow. Some idea of the colouring power of lead chromate may be obtained by observing the decided yellow precipitate, which is separated from a solution in which the dichromate colour is hardly discernible. Test analyses :—

5	10	20 c.c. 2N.NaHO excess.
0·0962	0·1000	0·0993 Mo recovered.

Attempts have been made to reduce the small amounts of CrO_3 so that they might be removed in one operation with the chromic hydrate. A great number of reducing agents are inactive to soda chromate in alkaline (soda) solutions, and such as are active introduce a greater error than they obviate by causing some of the molybdenum to be also precipitated.

An attempt made to precipitate molybdenum from a solution of chromic chloride in the cold showed that if lead acetate were added to a slightly acidified (HCl) solution, and then ammonium acetate, the lead molybdate comes down as a beautiful lustrous precipitate, and on continuing to add the acetate is re-dissolved. The heated solution turns milky, and on nearing boiling point deposits a dense faintly green precipitate. The circumstance of its formation suggests that this precipitate may be a definite compound. So far, however, no quantitative analysis has been made. This precipitate, after boiling for some ten or fifteen minutes, contains the whole of the molybdenum, and when ignited has generally a grey colour.

In adopting this way of analysing a chrome molybdenum compound, the ordinary acid precipitation is followed until the ignited grey precipitate is obtained. This is then boiled with hydrochloric acid, and ignoring a dark coloured insoluble powder (Cr_2O_3), the lead molybdate is re-precipitated and re-dissolved in soda hydrate as previously described. This is a more expeditious means of analysing chrome-molybdenums than any other I have tried. Test analyses :—

0·1	0·2 grm. Cr added.
0·1005	0·1002 Mo recovered.

The "acid precipitation," which has been so conspicuously successful and reliable under widely varying circumstances, may be advantageously adopted for estimating Mo in solutions of pure alkaline molybdates. Its chief recommendation is the fact that the form of the precipitate is more conducive to rapid filtering and washing. In the moist state its colour is more distinctly creamy than when precipitated in the usual way, and this creaminess might unwittingly be mistaken for evidence of chromate. After ignition, however, the precipitate has the usual colour of pure $PbMoO_4$.

Phosphoric Acid.

The estimation of molybdenum as lead molybdate in presence of salts of this acid at once suggests difficulties, due either to the formation of lead phosphate or of phosphomolybdates. The first of these compounds is by far the more formidable, and has occasioned more trouble than any other body dealt with.

Adrian and Trillat (*Journ. de Pharm. de Chim.*, vol. vii., No. 11; Chemical News, lxviii., 255) point out that phosphoglycerates are distinguished from neutral and acid phosphates by—amongst other things—the solubility of its lead salt in acetic acid. An attempt was made to utilise this feature as a means of holding the phosphoric acid in solution. This it is easily possible to do, so long as only salts of lead and phosphorus are present, but the precipitation of molybdenum invariably disturbed the equilibrium, and carried down large amounts of lead phosphate.

The want of success with this method is to be ascribed to ignorance of the precise conditions under which this property of phosphoglycerates can be successfully taken advantage of rather than to any inherent impossibility. When an interfering element has to be eliminated in the above way, nothing short of a thorough examination of every possible way of performing the operation can support the conclusion that the elimination is impossible. Such great care became unnecessary by the opening of a new and more promising course. It is well, however, to put on record the fact that lead molybdate may be accurately precipitated from solutions containing large amounts of glycerine.

On applying the "acid precipitation" to a solution containing 2 or 3 decigrms. of soda phosphate it was found that about 80 per cent of the phosphate had passed into solution. This appears to be chiefly due to the fact that acid phosphate of lead ($PbHPO_4$) is soluble in ammonia chloride. On re-dissolving the ignited precipitate and destroying the free HCl with ammonia acetate, the formation of the lead molybdate is preceded by the yellow phosphomolybdate. This interference is visible if there is the least delay during the addition of the acetate, and is probably present in a degree however the acetate be added.

Already there was evidence that here we were dealing with one of those cases in which the order of performing the operation was of great importance. This much can usually be surmised from the results of an experiment in which the estimated element is added last. Thus, here, to the clear solution containing soda phosphate, lead acetate, ammonia chloride, and the excess of ammonium acetate used to decompose the HCl, there was added 1 decigrm. of Mo. The result was less than 2 per cent too high. This order, of course, cannot possibly be imitated in practice, but the experiment usually fixes the high water mark of precision obtainable in any other way.

The plan finally adopted was to add to the solution containing the Mo and P salts enough HCl to prevent the formation of a precipitate on the subsequent addition of more than enough lead acetate to combine with the molybdic and phosphoric acids as $PbMoO_4$ and $PbHPO_4$ respectively.* This heated solution is then poured into another hot solution containing more than enough ammonium acetate to decompose the HCl, and from 10 to 15 grms. of ammonium chloride. The lower flask, which is violently shaken during the operation and for a little while afterwards, is digested for a few minutes and the solution filtered. The filtrate must be tested for excess of lead acetate by adding a drop of molybdate solution. The reverse order, addition of more lead acetate, always leads to a precipitate if much phosphate was originally present. Prolonged boiling of the clear filtrate may also lead to a precipitate if the acid lead phosphate was present in

* The more desirable way—addition of HCl to dissolve the combined precipitates of phosphate and molybdate—leads to the formation of phosphomolybdates in the hot, and is interfered with by the formation of lead chloride in the cold solution.

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greater amount than could be comfortably dissolved by the ammonium salts, but I have never found such a precipitate to contain more than the merest traces of molybdenum. The precipitate is the most easily filtrable of any yet met. Indeed it was desirable, in order to get a head of wash water, to use a funnel with a constricted stem.

The ignited precipitate may or may not contain phosphorus according to the amount originally present. With 0·3 grm. of soda phosphate along with 0·1 grm. of molybdenum, the first precipitate calculated to Mo gave, in two separate cases, 0·1060 grm. If such considerable amounts of phosphorus are being dealt with, the precipitation must be repeated by simply dissolving in HCl, and adding as before to a mixture of ammonium acetate and chloride. The same two precipitates after this operation gave 0·1000 and 0·0996 grm. of Mo respectively. A similar estimation in a solution containing 0·6 grm. of soda phosphate gave 0·1003 grm. of molybdenum.

These precipitates may be tested for phosphates by dissolving in hydrochloric acid and gently adding dilute ammonia. Just before lead molybdate would form, if more ammonia were added, the yellow phosphomolybdates will form if phosphates are present, or ammonia may be straightway added in excess and the precipitate carefully re-dissolved in nitric acid.

Where the lead phosphate present amounts only to 1 or 2 per cent of the weight of the ignited precipitate, it has been found to be very approximately accurate to complete the precipitation of the phosphomolybdate by shaking, filter through pulp, ignite, and from the formula $P_2O_5(Mo_6O_{17})_4$, containing 1·75 per cent P, to calculate the P to $Pb_3(PO_4)_2$ and subtract from the weighed $PbMoO_4$.

(To be continued).

A CHLORO-IODIDE OF TIN.

By C. LENORMAND.

In a preceding communication I have already mentioned, among the compounds formed by a metal united at the same time with several halogen elements, the existence of a new chlorobromide,—that is to say, a chlorobromide of iron. I now describe another of these compounds, a chloro-iodide of tin, obtained by the action of iodine on anhydrous protochloride of tin.

Iodine, at the normal temperature, has no very sensible action on anhydrous protochloride of tin; but at the same time crystals of iodine placed in contact with this salt gradually disappear, and we notice a coloured product form, which gradually gives the surface of the protochloride a bright red hue.

If a mixture of iodine and anhydrous chloride of tin in excess is heated in an open tube over a gas flame, an energetic reaction takes place; the iodine disappears and one portion of the mass becomes liquid, while abundant yellow fumes escape into the atmosphere. Finally the unattacked protochloride remains as residue.

If we conduct the operation, as I did in the case of ferric chlorobromide, in sealed tubes at 100°, the reaction is less vigorous and less rapid, but is complete at the end of a few hours,—above all, if we take care to shake up the tubes from time to time, so as to bring the unattacked chloride into contact with the remaining iodide. On cooling, a bright red, mobile, and dense liquid is found in the tubes, in which the excess of protochloride of tin, necessary to use, is found: this can be separated by decantation.

Analysis shows that the liquid thus obtained is a chloro-iodide of tin.

For estimating the tin in this body I did not use M. Ladenburg's method by which he obtained the chlorobromide $SnCl_2Br_2$, nor that of M. Classen, which consists in determining the tin by the electrolytic method. I was able to work in a more simple manner by taking advantage of the action of water on this substance. When thrown into water, in fact, this latter causes a precipitate, which dissolves gradually, but more quickly on agitation. The diluted solution is decomposed by heat; even at 65° all the tin is found to be precipitated in the state of gelatinous stannic hydrate, at the same time the iodine and the chlorine remain in solution in the form of hydriodic and hydrochloric acids. I weighed the tin as stannic oxide, this being obtained by the estimation of the precipitated hydrate. The chlorine and iodine were weighed by Rose's method. The following are the results:

	Calculated. $SnCl_2I_2$.	Found.		
Tin	26·63	26·78	26·50	26·77
Chlorine	16·00	15·84	15·91	15·91
Iodine	57·37	57·31	54·48	57·29
	100·00	99·93	99·89	99·97

This compound corresponds with the formula $SnCl_2I_2$, —that is, a chloro-iodide of tin.

This body is a bright red and very mobile liquid, giving off abundant yellowish fumes, but still fuming less than does stannic chloride. Its density at 15° is 3·287. When poured into a small quantity of water it gives off a considerable quantity of heat, forming a certain hydrate which we propose to examine later on, and which is soluble in an excess of water. If poured into ether chloro-iodide of tin gives rise to the formation of an insoluble compound, accompanied by a rise of temperature. Ethylic, propylic, butylic, and amylic alcohols cause the same phenomena, crystallised compounds being formed. It is soluble in benzene, sulphide of carbon, and chloroform.

Heat has a curious action on chloro-iodide of tin; when heated the liquid commences to distil over at 191°; after this the temperature can be increased without any change, and a wine-red liquid comes over. At about 297° the temperature does not increase and distillation stops.

If the residue and the distilled liquid be analysed, we find the stannic iodide in the retort, and in the recipient a mixture of three elements—viz., tin, chlorine, and iodine—containing all the chlorine of the original chloro-iodide.

The actual figures were, for 100 grms. distilled, 55·44 grms. found in the residue, and 44·55 grms. in the distilled liquid.

The analysis of the 55·44 grms. of residue gave as result:—

	Calculated for 55·44 per cent SnI_4.	Found.			Mean.
Tin	10·45	10·25	10·38	10·36	10·33
Iodine ..	44·98	44·94	44·87	44·99	44·93
Chlorine ..	0·00	0·00	0·00	0·00	0·00
	55·43	55·19	55·25	55·35	55·26

Thus the residue found in the retort corresponds well with the formula SnI_4 of stannic iodide.

The analysis of the 44·55 grms. of the distilled liquor was as follows:—

				Mean.
Tin	16·62	16·54	16·59	16·58
Iodine ..	12·43	12·40	12·35	12·39
Chlorine ..	15·58	15·67	15·79	15·68
	44·63	44·61	44·73	44·65

If we add together the tin, the iodine, and the chlorine of these two analyses, we arrive at the following results:—

	Residue.	Distillate.	Total.
Tin	10·33	16·58	26·91
Iodine	44·93	12·39	57·32
Chlorine	0·00	15·68	15·68
			99·91

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from which it is at once seen that all the chlorine contained in the 100 grms of the original chloro-iodide passed over in the distillation. But this is not all.

If the 44·55 grms. of the distilled liquor be submitted to a fresh distillation, it can be seen that boiling does not occur until the temperature reaches 140°, and that the temperature continues to rise until it becomes stationary at about 297°, while stannic iodide, SnI_4, still remains in the retort.

On further distillation an analogous phenomenon takes place, but the boiling-point goes down to 124° the while the distillation proceeds, the temperature again stops at about 297°, and we again find stannic iodide, SnI_4, in the retort.

This operation may be carried out a third and a fourth time, and the same results will be found, but the quantities of SnI_4 gradually decrease as the boiling-point becomes less.

Finally, on the fifth rectification, the substance only boils at 116°, and the retort contains only stannic iodide, while the liquid distilled contains all the chlorine which was first combined in the state of stannic chloride.

In 100 parts of $SnCl_2I_2$ originally distilled I found in the fifth distillation an amount of chloride of tin equal to 26·82, while 14·26 was the quantity of chlorine present.

The decomposition should take place according to the equation $2(SnCl_2I_2) = SnCl_4 + SnI_4$. In fact, for 100 grms. of $SnCl_2I_2$ we get theoretically 70·6 grms. of SnI_4 and 29·4 of $SnCl_4$.

Now, I have found after my repeated rectifications 67·78 of SnI_4 and 26·82 of $SnCl_4$, numbers which are sufficiently close to theory, *i. e.*, 70·6 and 29·4. I say *close*, inasmuch as during the five successive distillations a certain quantity of the liquid distilled is bound to be lost.

As I have already said, the final decomposition takes place according to the formula already given, but it cannot now be said what formulæ govern the intermediate reactions. Stannic iodide is left as a residue at each distillation; this substance is not volatile at the temperatures at which I have worked: how, then, can the iodine pass over by distillation? It seems probable that we must admit the existence of an intermediate dissociable and volatile chloro-iodide of tin. In any case this point seems to have a certain amount of interest, and I hope soon to forward a further communication.—*Journ. de Pharm. et de Chim.*, 1898, Series 6, vol. viii., No. 6.

DERIVATIVES OF THE TETRACHLORIDES OF ZIRCONIUM, THORIUM, AND LEAD.*

By J. MERRITT MATTHEWS.

1. Introduction.

The tetrachlorides of several of the members of Group IV. have been studied in their deportment with certain organic nitriles and amines, and the results seem to indicate that there is a general tendency toward reactions between these tetrachlorides and the latter-named reagents, giving rise to definitely constituted compounds. That is to say, the tetrachlorides of Group IV. appear to possess an acidic character in their ability to combine with certain organic bases to form neutral salts. This behaviour has already been studied with reference to the tetrachlorides of carbon, silicon, titanium, and tin; and although the data at our command are neither as connected nor as complete as might be desired, nevertheless, they may be regarded as sufficient to establish a characteristic group reaction. In these reactions, however, there appear to be several unaccountable fluctuations and divergences among the different members of the group. It would be natural to expect a difference in the behaviour of the metallic sub-group including germanium, tin, and lead, from the more non-metallic sub-group including titanium, zirconium, and thorium. But such a conclusion does not appear to receive the necessary strength from the actual facts observed in order to give it a sure foundation; for titanium seems to exhibit a greater analogy in its reactions to those of tin than to any other. The number of reactions studied, however, have been so few that it would be presumptuous to formulate a comprehensive law regarding the general reactions of the two sub-groups in question, and in consequence of their being no such law established, it would be illogical to argue that apparently diverging reactions pointed necessarily to inconsistencies in the behaviour of the two sub-groups.

The tetrachlorides of silicon, titanium, and tin have been rather comprehensively studied in their behaviour toward nitriles and amines. Titanium tetrachloride has been found to be reactive with formonitrile, acetonitrile, benzonitrile, toluonitrile, succinonitrile, chlorcyanogen, sulphur monochloride, phosphorus pentachloride, and the vapours of aqua regia. The tetrachloride of tin also exhibits analogous reactions with every one of the above mentioned reagents; silicon tetrachloride, however, shows no evidence of reacting with these compounds.

All three of these tetrachlorides give derivatives with ammonia and aromatic amines, as does also carbon tetrachloride. With the fatty amines, however, only the chlorides of silicon and tin have been found to be reactive.

2. Preparation of the Tetrachlorides of Zirconium, Thorium, and Lead.

A. *Zirconium Tetrachloride.*

The zirconium tetrachloride used in this research was prepared in the following manner:—Carefully selected crystals of zircon were finely powdered and fused with acid potassium sulphate; the fusion was lixiviated with water and filtered; the residue was dried and fused with potassium hydroxide in a nickel dish. This fusion, after being digested with water and filtered, left a white amorphous residue of zirconium dioxide. The oxide was mixed with pulverised starch and molasses to a thick batter, which was then rolled into small pellets about 1 c.m. in diameter. These were slowly dried in an air oven until all moisture was expelled, when they were transferred to a covered silver crucible and charred until no more vapours were evolved. These pellets, containing zirconium dioxide intimately mixed with pure charcoal, were placed in a long glass combustion tube, and strongly heated in a current of dry chlorine gas. Zirconium tetrachloride was formed by this procedure, and collected in the cooler part of the tube in the form of a white powder or minute crystals. The salt thus obtained was dissolved in ether which had been carefully dehydrated by repeated distillation over sodium, until thin slices of the metal remained untarnished on being in contact with the ether for several days. The zirconium tetrachloride in the form of this ethereal solution was used in all the experiments, as it gave a convenient and uniform method for testing the reactions.

B. *Thorium Tetrachloride.*

This salt was prepared in a manner precisely analogous to that given for zirconium. The dioxide, ThO_2, was obtained from a quantity of the nitrate which was available for the purpose by precipitation with ammonium hydroxide and subsequent ignition. The tetrachloride was dissolved in dehydrated ether, as in the case of the zirconium salt, and this solution was used in all of the reactions.

C. *Lead Tetrachloride.*

This compound was prepared by the method of Friedrich (*Ber. d. Chem. Ges.*, xxvi., 1434). One part of lead chloride was suspended in twenty parts of concentrated hydrochloric acid, and a current of chlorine gas was conducted

* Contribution from the John Harrison Laboratory of Chemistry. From the *Journal of the American Chemical Society*, xx., No. 11. From author's thesis for the Degree of Doctor of Philosophy.

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hrough the liquid until nearly all of the lead dichloride had gone into solution, which required about twenty hours. The temperature of the liquid during the entire process was kept at about 4° C. by means of a freezing mixture. The yellow-coloured liquid which resulted from this treatment consisted of a solution of lead tetrachloride in concentrated hydrochloric acid. Two parts of ammonium chloride dissolved in ten parts of water were then added, and a bright lemon-yellow crystalline precipitate was produced, consisting of the ammonium double salt of lead tetrachloride, which, according to Friedrich, has the formula $PbCl_4 \cdot 2NH_4Cl$. Classen and Zahorski (*Ztschr. Anal. Chem.*, iv., 100), however, apparently obtain the same salt—by practically the same method—and they ascribe to it the formula $2PbCl_4 \cdot 5NH_4Cl$. The ammonium double salt was filtered off and washed free from hydrochloric acid and chlorine with absolute alcohol and ether. A portion of this salt was placed in a separatory funnel and digested with fuming sulphuric acid of specific gravity 1·879. A brisk reaction took place, and yellow oily drops of lead tetrachloride soon separated out; these were washed by decantation several times with fuming sulphuric acid, and finally dissolved in chloroform which had been carefully dehydrated over fuming sulphuric acid. This chloroform solution of the lead tetrachloride was used for all the reactions; but fresh portions and solutions had to be made for each experiment, as the tetrachloride decomposed into the lower chloride in a few hours. It was found impossible to work with the liquid tetrachloride itself, as it was immediately decomposed on coming in contact with the air, and even decomposed in about twelve hours when kept under fuming sulphuric acid. The strength of the acid used for the decomposition of the ammonium double salt is an important factor in this preparation, as an acid of less strength than that used above will fail to give the lead tetrachloride in any appreciable quantity.

3. The Action of Nitriles, &c., on the Tetrachlorides.

As zirconium occupies the next position to titanium in the same sub-group, it was natural to suppose that its tetrachloride would exhibit reactions with the nitriles somewhat analogous to those of the latter element, and that the analogy might also be followed into the fatty and aromatic amines. Contemporary with this present work there was carried to completion in this same laboratory a study of the reactions of silicon tetrachloride; and as both tin and titanium have been studied in this same connection, it was considered that a research into the possible derivatives of the allied members of this group might lead to results which would be useful in establishing analogies and comparisons between the different members of Group IV., as viewed from their respective behaviour with the reagents used in this study. By this means it was thought probable that a definite law might be formulated for the group with regard to these reactions, and that the heterogeneous data, heretofore lying dissociated and useless, might be brought together and systematically understood.

a. Vapours of Aqua Regia.—The dry vapours of aqua regia conducted into the solution of zirconium tetrachloride gave no reaction, the solution only becoming discoloured by the gases, which were again liberated on raising the temperature. Portions of the dry zirconium salt were also placed in a porcelain boat, and heated in a current of the dry vapours of aqua regia; but the salt appeared to volatilise unchanged, and no compound was formed. In this behaviour zirconium shows a deviation from that of titanium, as the tetrachloride of the latter reacts readily with the vapours of aqua regia, giving a compound corresponding to the formula $3TiCl_4 \cdot 2NO_2Cl$, Hampe (*Ann. Chem., Liebig*, cxxvi., 43). An analogous compound with tin tetrachloride has been prepared by the same investigator. Baeyer (*Ber. d. Chem. Ges.*, vii., 1639) also records the compound $SnCl_4 \cdot 2NOCl$.

The solutions of the tetrachlorides of thorium and lead behaved similarly to that of zirconium, and gave no derivatives.

b. Nitrogen Dioxide.—This gas, obtained by heating lead nitrate, on being conducted into the solutions of the tetrachlorides, gave no reaction beyond a simple solution of the gas. The dry salts of zirconium and thorium, heated in a current of the gas, volatilised unchanged and gave no compound.

c. Sulphur Monochloride.—On mixing this substance with the solutions of the tetrachlorides no reaction was observed.

d. Chlorides of Phosphorus.—The action of both the tri- and pentachlorides of phosphorus was tried on the solutions of the tetrachlorides, but no combination resulted.

e. Dicyanogen.—On conducting this gas into the solutions of the tetrachlorides no reaction took place; nor does it seem to have formed any compounds with the corresponding salts of titanium or tin.

f. Formonitrile.—Though both titanium and tin tetrachlorides give derivatives with hydrocyanic acid, yet no product was obtained by allowing this compound to act on the three tetrachlorides here investigated.

g. Cyanogen Chloride.—It was prepared by the action of chlorine on mercuric cyanide, but it gave no reactions with the solutions of the tetrachlorides.

h. Acetonitrile.—The vapours of this nitrile passed into the solutions of the tetrachlorides yielded no compounds, although derivatives have been obtained with the titanium and tin salts.

i. Benzonitrile.—Like acetonitrile, this aromatic body yielded no derivatives with the tetrachlorides.

Summary.

From these experiments it is to be observed that the nitriles and the other reagents here used, which for the most part gave additive compounds with the tetrachlorides of titanium and tin, are without action on the corresponding salts of zirconium, thorium, and lead.

(To be continued).

PROCEEDINGS OF SOCIETIES.

CHEMICAL SOCIETY.

Ordinary Meeting, December 15th, 1898.

Professor Dewar, F.R.S., President, in the Chair.

Certificates were read for the first time in favour of Messrs. Stuart Blofeld, 4, Camden Gardens, West Kensington Park, W.; Bertram H. Bowles, 53, Dunsmure Road, Stamford Hill, N.; Thomas John Cheater, 6, Boutflower Road, Wandsworth Common, S.W.; George Ward Hedley, 2, St. Luke's Villas, Cheltenham; Harold Octavius Knight, Westfield Villa, Barton-on-Humber; Dudley Northall-Laurie, 56A, Pall Mall, S.W.; James McCracken, 580, Govan Road, Govan, N.B.; John O'Sullivan, 742, Nicola Street, Vancouver City, B.C.; Arthur Lee White, 29, Huron Road, Upper Tooting, S.W.

Mr. H. P. Bell was formally admitted a Fellow of the Society.

The following papers were read:—

147. "*The Interaction of Ethylic Sodiomalonate and Mesityl Oxide.*" By Arthur W. Crossley.

Attempts to prepare dihydrocamphoric acid synthetically have so far proved unsuccessful (*Trans.*, 1898, lxxiii., 23). Isobutylene dibromide does not condense with ethylic sodiomethylmalonate, nor mesityl oxide with ethylic sodiomalonate, in the expected manner. The thick, oily product obtained in the latter case cannot be distilled in a

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vacuum without partial decomposition; when hydrolysed with alcoholic potash it yields a dibasic *acid*, $C_{16}H_{24}O_4$, which crystallises from acetone in colourless, transparent, lustrous prisms belonging to the monosymmetric system, and melts at 148—148·5°, the upper part of the capillary tube becoming covered with a red film. The *ethylic* salt separates from light petroleum in thick, transparent, lustrous prisms, which usually are twinned, and apparently belong to the monosymmetric system. It melts at 59·5—60°, boils at 252° in air without decomposition, and, on hydrolysis, yields the original acid. The *silver* salt crystallises from water in feathery needles.

Sodium amalgam is without action on the acid. Bromine readily converts it into a *dibromo*-derivative, $C_{16}H_{24}O_4Br_2$ or $C_{16}H_{22}O_4Br_2$, which crystallises from dilute alcohol in colourless, glistening leaflets containing $2H_2O$, and melts with slight decomposition at 171°. On treatment with hydrogen bromide, a *dihydrobromide*, $C_{16}H_{26}O_4Br_2$, is obtained, which crystallises in transparent prisms, melts at 169° with decomposition, and is re-converted into the acid, $C_{16}H_{24}O_4$, by interaction with alcoholic potash.

The acid is readily oxidised by alkaline potassium permanganate in the cold, and when the product is treated with chromic acid an acid melting at 89° is obtained. It is hoped that a study of its oxidation products will give some clue to the constitution of the substance.

148. "*The Interaction of Ethylic Malonate and Acetylene Tetrabromide in presence of Sodium Ethoxide.*" By Arthur W. Crossley.

This investigation was undertaken in the hope that ethylic disodiomalonate and acetylene tetrabromide would interact according to the equation,—

$$C_2H_2Br_4+2Na_2C(CO_2Et)_2=$$
$$=(CO_2Et)_2C:CH\cdot CH:C(CO_2Et)_2+4NaBr,$$

as the product, on hydrolysis and subsequent heating, should yield muconic acid, $CO_2H\cdot CH:CH\cdot CH:CH\cdot CO_2H$, from which tetrabromadipic acid could be prepared for the purpose of investigating its behaviour with weak alkalis.

The reaction does not take place as expected, and is of a complicated nature, the two main products being tribromethylene, $CHBr:CBr_2$, and tetrethylic acetylenetetracarboxylate; during its progress acetylene is given off, and tarry products are also formed from which no definite chemical compound could be isolated.

The acetylene tetrabromide used was prepared from acetylene generated from calcium carbide by the action of water, and purified by Willgerodt's method (*Ber.*, 1895, xxviii., 2108). It boiled at 151° under 54 m.m. pressure, and was a clear, colourless, highly refractive liquid.

0·1548 gave 0·3353 AgBr. Br=92·18.
$C_2H_2Br_4$ requires Br=92·48 per cent.

Acetylene tetrabromide (1 mol.) was added to a mixture of sodium (2 mols.) dissolved in absolute alcohol and ethylic malonate (2 mols.), and after the violent reaction had somewhat moderated, the whole was heated on a water bath for 1½ hours. Water was added to the resulting dark, reddish green, feebly-acid product, and the whole extracted with ether. On washing the ethereal extract with water, the greater portion of the red colouring matter (from which the tarry products alluded to were obtained) was removed, and also a small quantity of a green solid containing sodium and organic matter. When boiled with acids this green substance partially dissolved, forming a red solution, which was again turned green by addition of an alkali; but the amount was too small for investigation. On distilling the residue from the dried ethereal extract, fractions were obtained boiling at 65—80° and at 225—230° under 47 m.m. pressure, and not more than 0·5 c.c. passed over between these limits.

The fraction boiling at 65—80° under 47 m.m. pressure contained tribromethylene, $CHBr:CBr_2$. This clear, colourless, heavy liquid, amounting to 63 per cent of the total ethereal extract, was repeatedly fractionated at the ordinary pressure, and nearly the whole passed over between 164—166°; the residue, when heated above this temperature, gave off bromine and hydrogen bromide, and consisted probably of some unchanged acetylene tetrabromide. On analysis the fraction boiling at 164—166° gave the following numbers:—

0·3410 gave 0·7251 AgBr. Br=90·47.
$CHBr:CBr_2$ requires Br=90·56 per cent.

The substance was further characterised by converting it into pentabromethane by the direct addition of bromine. The resulting solid crystallised from alcohol in long, white, glistening needles melting at 55—55·5°.

0·2656 gave 0·5887 AgBr. Br=94·31.
$CHBr_2\cdot CBr_3$ requires Br=94·11 per cent.

The fraction boiling at 225—230° under 47 m.m. pressure contained tetrethylic acetylenetetracarboxylate. This fraction solidified almost completely. It was spread on a porous plate, and then purified by re-crystallisation from light petroleum boiling at 60—80°, from which it separated in long, white, silken needles melting at 75—76°.

0·1518 gave 0·2936 CO_2 and 0·0940 H_2O. C=52·76; H=6·87.
$(CO_2Et)_2CH\cdot CH(CO_2Et)_2$ requires C=52·83, H=6·91 per cent.

Although the conditions under which the reaction was carried out were varied to some extent, the same results were always obtained.

149. "*Derivatives of Camphoric Acid.*" Part III. By F. Stanley Kipping, D.Sc., F.R.S.

This paper contains an account of the preparation, properties, and transformations of a number of compounds which have been obtained from π-bromocamphoric acid, and is a continuation of previous work (*Trans.*, 1896, lxix., 913; Kipping and Pope, *Trans.*, 1897, lxxi., 963).

ππ-Dibromocamphoric acid, ππ-dibromocamphoric anhydride, and π-bromocamphanic acid have been already briefly described (*Proc.*, 1895, xi., 211).

ππ-Chlorobromocamphoric anhydride,—

$$C_8H_{12}ClBr\begin{matrix}CO\\CO\end{matrix}>O,$$

is obtained by treating π-bromocamphoric acid with phosphorus pentachloride, and then passing chlorine into the product heated at 100°. It crystallises in large, orthorhombic prisms melting at 214—215°, and resembles the corresponding dibromo-compound in ordinary properties.

ππ-Chlorobromocamphoric acid, $C_8H_{12}ClBr(CO_2H)_2$, can be prepared by heating its anhydride with concentrated nitric acid; it is a colourless, crystalline compound melting at about 197°, and is very like the dibromo-acid in all respects.

When ππ-chlorobromocamphoric anhydride is boiled with dilute acetic acid it is converted into a π-bromocamphanic acid, identical with the compound melting at 176—177°, obtained by the decomposition of ππ-dibromocamphoric anhydride.

Methylic π-bromocamphanate,—

$$CO_2Me\cdot C_8H_{12}Br\begin{matrix}CO\\|\\O\end{matrix},$$

is easily obtained from the corresponding acid by the ordinary methods; it crystallises in orthorhombic prisms, melts at 87—88°, and dissolves freely in most of the ordinary organic solvents.

π-Bromocamphanamide,—

$$NH_2\cdot CO\cdot C_8H_{12}Br\begin{matrix}CO\\|\\O\end{matrix},$$

is produced when ππ-dibromocamphoric anhydride is left in contact with aqueous ammonia, and can also be prepared from methylic π-bromocamphanate in a similar

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manner; it crystallises in transparent needles melting at 161—162°.

The action of alkalis on πw-dibromocamphoric anhydride results in the formation of hydroxy-*cis* π-camphanic acid (*Trans.*, 1896, lxix., 913), but when the anhydride is heated with an aqueous solution of silver nitrate, it is partly converted into the γ-lactone of hydroxycamphotricarboxylic acid (*loc. cit.*); the last-named compound is also formed when π-bromocamphanic acid is boiled with an aqueous solution of silver nitrate.

150. "*Synthesis of αββ-Trimethylglutaric Acid.*" By W. H. Perkin, jun., and J. F. Thorpe.

This acid, which is especially interesting on account of the fact that Balbiano (*Ber.*, 1895, xxviii., 2161) obtained it by simple reactions from camphoric acid, may be prepared synthetically in the following way.

Ethylic cyanacetate is digested in alcoholic solution with sodium ethylate and ethylic dimethylacrylate, and the product, which contains the sodium compound of *ethylic α-cyano-ββ-dimethylglutarate*,—

$$CO_2Et(CN)CNa\cdot CMe_2\cdot CH_2\cdot CO_2Et,$$

is treated with methylic iodide. The resulting *ethylic α-cyano-αββ-trimethylglutarate*,—

$$CO_2Et(CN)CMe\cdot CMe_2\cdot CH_2\cdot CO_2Et,$$

a colourless oil boiling at 181° under 25 m.m. pressure, yields on hydrolysis *αββ-trimethylglutarimide*,

$$CMe_2\begin{matrix}CH_2-CO\\CHMe\cdot CO\end{matrix}NH,$$

which crystallises in long needles and melts at 126°.

αββ-Trimethylglutaric acid,—

$$CO_2H\cdot CHMe\cdot CMe_2\cdot CH_2\cdot CO_2H,$$

is obtained from this imide by heating with hydrochloric acid at 200°; it melts at 88°, gives an *anhydride* melting at 82°, and an *anilic acid* melting at 150°, and is, in all its properties, identical with the acid obtained from camphoric acid by Balbiano.

151. "*Hydrolysis of Methylic and Ethylic γ-Cyanoacetoacetates and their Derivatives.*" Part I. By W. Trevor Lawrence.

A preliminary account is given of the results obtained in an investigation which had, for its primary object, the preparation of unsymmetrically disubstituted ethylic acetonedicarboxylates, but has led to the discovery of a new series of acids.

Methylic γ-cyanodimethylacetoacetate,—

$$CN\cdot CH_2\cdot CO\cdot CMe_2\cdot CO_2Me,$$

is the chief product of the interaction of methylic γ-bromodimethylacetoacetate with potassium cyanide in ethereal solution. It boils at 126—128° under 18 m.m. pressure. On treatment in ethylic alcohol solution with dry hydrogen chloride it yields an oil,—

$$CO_2Et\cdot CHCl\cdot CO\cdot CMe_2\cdot CO_2Et,$$

which boils at 146—150° under 40 m.m. pressure, and when hydrolysed with concentrated hydrochloric acid is converted into *αα*-dimethyl-*β*-hydroxyglutaconic acid. Sodium amalgam does not reduce the nitrile under the varied conditions employed, but converts it into dimethylmalonic acid.

Methylic γ-cyanodimethylacetoacetate is hydrolysed rapidly by concentrated hydrochloric acid, and converted quantitatively into a substance which is regarded provisionally as *αα-dimethyl-β-hydroxyglutaconic acid*,—

$$CO_2H\cdot CH:C(OH)\cdot CMe_2\cdot CO_2H,$$

although several of its reactions are difficult to explain if the formula adopted is correct. Thus, the compound remains unchanged on boiling with sulphuric and with nitric acids, is not affected by potassium permanganate at 60°, and gives no colouration with ferric chloride. The acid crystallises from water in prisms, melts at 214°, and distils at 245°. The *hydrogen silver* salt, $C_7H_9O_5Ag$, and the corresponding *copper* and *zinc* salts have been obtained. The *aniline* salt melts at 122°. The *dimethylic* salt, $CO_2Me\cdot CH:C(OH)\cdot CMe_2\cdot CO_2Me$, crystallises in needles, melts at 104°, and boils at 285°. The *acetyl* derivative melts at 136°, and the *benzoyl* derivative at 208°. When the acid is treated with phosphorus pentabromide and the product poured into methylic alcohol, the methylic salt of a bromo-derivative is obtained which, on hydrolysis with hydrobromic acid, yields *αα*-dimethylglutaconic acid.

αα-Dimethylglutaconic acid,—

$$CO_2H\cdot CH:CH\cdot CMe_2\cdot CO_2H,$$

is also obtained by the reduction of dimethylhydroxyglutaconic acid with hydriodic acid at 130° in sealed tubes. It crystallises from water in prisms, melts at 148, and is not reduced by sodium amalgam in the cold.

The following compounds have also been prepared:—

Ethylic γ-bromomethylethylacetoacetate,—

$$CH_2Br\cdot CO\cdot CMeEt\cdot CO_2Et,$$

boiling at 164° under 75 m.m. pressure; *ethylic γ-cyanomethylethylacetoacetate*,—

$$CN\cdot CH_2\cdot CO\cdot CMeEt\cdot CO_2Et,$$

boiling at 158° under 35 m.m.; *αα-methylethyl-β-hydroxyglutaconic acid*, $CO_2H\cdot CH:C(OH)\cdot CMeEt\cdot CO_2H$, melting at 164°; *ethylic γ-bromodiethylacetoacetate*,—

$$CH_2Br\cdot CO\cdot CEt_2\cdot CO_2Et,$$

boiling at 180° under 100 m.m. pressure; *ethylic γ cyanodiethylacetoacetate*, $CN\cdot CH_2\cdot CO\cdot CEt_2\cdot CO_2Et$, boiling at 158° under 75 m.m. pressure; *αα-diethyl-β-hydroxyglutaconic acid*, $CO_2H\cdot CH:C(OH)\cdot CEt_2\cdot CO_2H$, melting at 159°.

Different results are obtained by the hydrolysis of these nitriles by means of sulphuric acid and of methyl alcoholic potash; moreover, the products of the reduction of the hydroxyglutaconic acids with hydriodic acid differ with the conditions. The author is engaged in investigating these reactions, as well as the behaviour of the γ-nitriles of ethylic acetoacetate and its derivatives generally.

NOTICES OF BOOKS.

Commercial Organic Analysis. A Treatise on the Properties, Proximate Analytical Examination, and Modes of Assaying the various Organic Chemicals and Products employed in the Arts, Manufactures, Medicine, &c., with Concise Methods for the Detection and Determination of their Impurities, Adulterations, and Products of Decomposition. By Alfred H. Allen, F.I.C, F.C.S., Past President of the Society of Public Analysts, Public Analyst for the West Riding of Yorkshire, the City of Sheffield, &c. Second Edition, Revised and Enlarged. Vol. IV.—Proteids and Albuminous Principles. London: J. and A. Churchill, 7, Great Marlborough Street.

With this volume Mr. Allen's extensive work is brought to a conclusion, its production having extended over fourteen years. The work is worthy of the author, and has already proved of great value to the profession.

In the Preface to this volume Mr. Allen regrets that he is unable to personally undertake the thorough revision of the earlier part of the work as he had originally intended, but proposes to publish an Appendix to each volume which shall include the more important facts that have accumulated during recent years. The partial revision of the earlier volumes is being undertaken by Dr. Henry Leffmann, of Philadelphia, and vol. I. is already published, while vol. II. will follow shortly.

Much of the matter in the present volume is of special practical interest, being the outcome of the author's analytical experience. Through the kindness of Dr. T.

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E. Thorpe, the Government method for analysing milk has been included in full detail; there is also a very complete article on the absorption spectra of hæmoglobin and its allies, followed by a full description of the spectroscopes and micro-spectroscopes used, with practical hints on their manipulation.

At the end of the book will be found Addenda to many of the articles, giving details of papers by different authors, bearing on subjects that have appeared in various journals up to the present date.

Throughout the work the high standard of excellence that characterised the first volume has been maintained.

Matter, Energy, Force, and Work. By Silas W. Holman. London and New York: The Macmillan Company.

This is a well thought out and carefully written treatise on the fundamental ideas of Physical Science. There is nothing absolutely novel in the book, yet as a whole it is a distinct advance on any work of its class that we have come across.

The author takes energy as his starting point, and shows that force and work, both internal and external, are functions of it. Further, starting from the demand of the kinetic theory of gases for a complex atom, and from the necessity of the idea of space being filled with something known as ether, he shows how the vortex-atom, so far as it has been mathematically investigated, fulfils both demands, and at the same time leaves energy in its position as the one unchangeable and indestructible function.

We can recommend this work to our readers as being well worth reading.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

Note.—All degrees of temperature are Centigrade unless otherwise expressed.

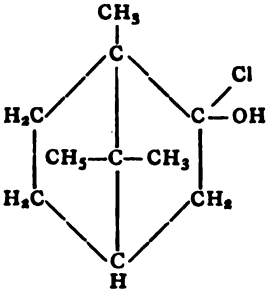
Comptes Rendus Hebdomadaires des Séances, de l'Académie des Sciences. Vol. cxxvii., No. 16, October 17, 1898.

A New Hydrate of Chromium.—G. Baugé.—This new oxide of chromium is capable of several stages of hydration. (1), $Cr_3O_4.H_2O$, obtained already by Peligot. (2), $Cr_3O_4.3H_2O$, a brownish yellow hydrate, which the author prepares very rapidly by closing one of the ends of the tube containing the brick-red hydrate mentioned below. The tube is then placed in boiling water, and the air pumped out until the hydrate loses some of its water. This substance is comparatively stable. (3), a brick-red unstable hydrate, of which the author's analyses have led him to suppose contains four molecules of water.

Action of Soda Ammonium on Arsenic.—C. Hugot.—The author, when acting upon phosphorus with soda ammonium, obtained different compounds if the phosphorus or the soda ammonium was in excess, but in his present research with arsenic he can only obtain the one compound $AsNa_3NH_3$. To prepare this latter substance the sodium and arsenic are both very pure. They are contained in one branch of a double sealed tube, which also contain liquid ammonia gas. A brick-red body is formed, which is slightly soluble in liquid ammonia gas, imparting to it a greenish yellow colour. On evaporating the ammonia very minute crystals are deposited.

Researches on Iodated Borates. — H. Allaire.—Chloroborate of magnesium, which constitutes natural boracite, can be considered as the starting point of a series of compounds of the same crystalline form, in which the chlorine can be replaced by iodine, and the magnesium by zinc, cadmium, manganese, nickel, cobalt, or iron. These compounds are prepared by acting with the vapour of the iodide of the metal on the corresponding borate, at a high temperature and in a current of carbon dioxide; on cooling, crystals of the boracite separate out. The author has prepared the following salts:— $6MgO.8B_2O_3MgI_2$, $6ZnO.8B_2O_3.ZnI_2$, $6CdO.8B_2O_3CdI_2$, $6MnO.8B_2O_3MnI_2$, $6NiO.8B_2O_3.NiI_2$, $6CoO.8B_2O_3.CoI_2$, $6FeO\ 8B_2O_3.FeI_2$.

Solubility of Camphor.—C. Israti and A. Zaharia.—The authors have observed, in the course of synthetic experiments with camphor, that the latter is soluble in water and in hydrochloric acid, which probably transforms it into its derivative—



by direct addition. If to the solution of camphor in concentrated hydrochloric acid a little water is added, a slight precipitate is produced, which dissolves in excess of the same liquid. This is probably due to separation of the body into camphor and hydrochloric acid, the camphor dissolving in excess of water. It is, however, stated by some that camphor is almost insoluble in water. The density of an aqueous solution of camphor at 15° has been found equal to 1·00071. This solubility has been confirmed by the polarimeter; an aqueous solution of camphor saturated in the cold, contained in a tube 22 c.m. long, gave $(\alpha)_D = 0·4°$. As regards the combination of camphor with hydrochloric acid, the body is decomposed by the least trace of water, but the melting-point (about 243°) is much lower than that of camphor. It was also observed that camphor was the most soluble in this acid in the cold.

Researches on Incandescent Electric Lamps charged with a Mixture of Marsh Gas and Air.—H. Couriot and J. Meunier.—A description is given of a method of introducing a mixture of marsh gas and air, in the most explosive proportions, into electric lamps during incandescence. It was found that the incandescence of the filament was at once obscured except at one point, where, in a minute or so, rupture occurred with a faint spark. In no case was there an explosion of the mixture of air and methane; but combustion had occurred, as was shown by the production of water and carbon dioxide, and the disappearance of inflammable gas inside the lamp. Hence the spark, which passed at the moment the filament was ruptured, remained without effect. It has previously been pointed out that incandescent metallic threads are powerless to cause the explosion of the most explosive mixtures; the same is the case with the lamp filaments.

No. 17, October 24, 1898.

Properties of Calcium.—Henri Moissan.—The author further examines the calcium, the preparation of which was announced in a previous paper. He determines the fusing-point of the metal, by heating it carefully and gradually in a vacuum, to be about 760°. On solidifying the liquid formed, a non-crystalline and soft form of calcium results. The density of the crystalline form is 1·85, whilst non-crystalline calcium sinks in propyl iodide of density 1·78, and floats in allyl iodide of density 1·87.

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The non-crystalline form scratches lead, but not chalk. Calcium crystallises in hexagonal plates or derived rhombohedra. With hydrogen the metal forms a crystalline hydride, CaH_2. Calcium is not attacked by chlorine in the cold, but at 400° the chloride is formed. It burns in oxygen at 300° with a brilliant light, and at a dull red heat, in a current of air, both the elements of the atmosphere are fixed. Water attacks calcium at ordinary temperatures, slaked lime being formed.

The Atomic Weight of Tellurium in relation to the Multiple Proportions of the Atomic Weights of other Simple Bodies.—H. Wilde.

Positions of Tellurium and Iodine in the Periodic System of the Elements.—H. Wilde.—These two papers are unsuitable for abstraction.

Calcium Amalgam.—T. Ferée.—The amalgam is very difficult to prepare and almost impossible to keep, owing to its rapid oxidation. The author has prepared small quantities of it by the electrolysis of the chloride, using a mercurial electrode or a porous diaphragm, separating the two electrodes, to prevent the action of the chlorine on the amalgam produced. To avoid rise of temperature in the vessel, cold water is kept circulating round it. The solid amalgam produced by this method is porous and whitish green in colour. It oxidises rapidly in the air and decomposes water. It appears to correspond to the formula Ca_3Hg_4. Heated in a current of hydrogen to a high temperature, it loses more mercury. When heated in a current of nitrogen the nitride is produced.

Action of Metallic Sulphates on Paratungstate of Potassium.—L. A. Hallopeau.—The author studies the double tungstates formed when solutions of metallic tungstates act on potassium paratungstate. He has obtained, by a careful preparation, (1) the paratungstate of potassium and magnesium,—

$$12WO_3.5(\tfrac{2}{3}K_2O + \tfrac{1}{3}MgO) + 24H_2O,$$

a crystalline body, which acts energetically on polarised light. It loses 17 molecules of water at 100°. (2) the paratungstate of potassium and manganese,—

$$12WO_3.3K_2O.2MnO + 16H_2O,$$

a yellowish-white solid, quite insoluble in water, also acting on polarised light.

Decomposition of a Normal Saturated Hydrocarbon by means of Aluminium Chloride.—C. Friedel and A. Gorgen.—One of the authors, in collaboration with J. M. Crafts, has notified, almost from the beginning of their researches on the syntheses effected by means of aluminium chloride, the decomposing action exercised by this reagent on certain hydrocarbons—*e.g.*, the decomposition (1) of hexamethyl-benzene into durene and other hydrocarbons; (2) of naphthalene into benzene, dinaphthyl, and hydrides of naphthalene; (3) of benzene (at a high temperature) into diphenyl, toluene, and other hydrocarbons. The present paper discusses the treatment of normal hexane with aluminium chloride. The hexane employed was prepared by decomposing propyl iodide with sodium, and also by treating mannite with hydriodic acid, and subsequently submitting the iodide thus obtained to the action of zinc dust. It was introduced in successive stages into the tube containing the aluminium chloride, first passing through a little tube containing bromine, to remove any trace of hexene. The mixture was warmed, and the products passed through a condenser into two U-tubes surrounded with ice, the first containing a little water to retain the hydrochloric acid evolved; the apparatus terminated in a vessel of mercury to collect gaseous products. Finally, a mobile liquid was obtained from the U-tubes, and fractionally distilled. It consisted of unchanged hexane, of pentane, and other more volatile hydrocarbons. The gas collected over mercury consisted chiefly of butane. Thus the action of $AlCl_3$ on hexane consists essentially in removing a CH_3 group, which is replaced by a hydrogen atom and yields pentane. The latter, in its turn, may be similarly converted into butane, which, on account of its volatility, would be but little transformed into propane. At the same time hydrocarbons, richer in carbon than hexane, are found by extracting the aluminium chloride with water.

Amines and Amides derived from Aldehyds.—Marcel Delépine.—In a series of previous papers the author has discussed, from a thermochemical point of view, a certain number of combinations engendered by the action of aldehydes on ammonia or certain amines. The general type of reaction is as follows:—

$$n \text{ aldehyd} + m \left\{ \begin{matrix} \text{ammonia} \\ \text{or amine} \end{matrix} \right\} = \text{new body} + p H_2O.$$

The author now classifies the data obtained, with a view to generalising, as far as is possible, from the substances studied.

Journal de Pharmacie et de Chimie, vol. vii., No. 12.

The Value of Tincture of Guiacum as a Test for Oxidising Agents.—Pierre Breteau.—Guiacum resin, which becomes blue on contact with certain oxidising agents, is specially recommended as a sensitive test for blood, sulphate of copper, hydrocyanic acid, phosphorus, &c., either by direct action or through the medium of essence of turpentine. The author has found that this blue colour will appear under circumstances not yet published, and hence errors may easily be made; the phenomenon of turning blue depends on conditions little understood, so that, by even slightly varying these conditions, the reagent can no longer be trusted,—for instance, according to Schœnbein, if equal volumes of tincture of guiacum and aerated turpentine mixed, are shaken up with water, the white precipitate takes an intense blue colour; but according to the author, if this is only slightly modified, and the aerated turpentine is added to a mixture of water and tincture of guiacum, the blue colour does not appear at all, even after prolonged agitation and increase of temperature. Another experiment of Schœnbein's was repeated with blood, using also pure distilled water and absolute alcohol, but no phenomenon occurred; but on the addition of a single drop of essence of turpentine the deep blue colour appeared immediately. It is also shown that traces of copper, which may possibly be present in distilled water, will cause the blue colour to appear without the intervention of essence of turpentine. And again, ordinary ether, alcohol, and benzene have sometimes been found to turn tincture of guiacum blue in the presence of essence of turpentine, while on other occasions, under apparently the same conditions, no colouration has been noticed,—doubtless the presence of copper or other impurities has been the cause of the colouration. Other experiments are described, using paper saturated with tincture of guiacum for the detection of phosphorus and hydrocyanic acid, in which it is shown that the apparent results may be quite misleading, if even only a trace of copper is present.

A Method of Estimating Nitrites in Waters.—Lucien Robin.—Already inserted in full.

Vol. viii., No. 1.

This number contains no matter of chemical interest.

No. 2.

The Hydrolysis of the Pectine of Gentian.—E. Bourquelot and H. Hérissey.—The experiments to which the authors have submitted the pectine of gentian have led to the production of mucic acid by the action of nitric acid, and the production of arabinose, by hydrolysis with the aid of dilute sulphuric acid. The treatment by nitric acid was applied to the pectine obtained by aqueous digestion at 110°, using 12 c.c. of nitric acid to 1 grm. of dried pectine: after heating on the water-bath until the volume is reduced to one-third, it is left to stand for twelve hours, to allow the crystals which form towards

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the end of the operation to collect: these are thrown on a double filter and washed with water, and dried first at 30°, then at 100°. The mucic acid formed melts at 215°. The hydrolysis of the pectine by dilute sulphuric acid is effected by keeping 10 grms. of pectine, 500 grms. of water, and 15 grms. of sulphuric acid at 110° for an hour and a half. It is allowed to cool, and filtered; it is then boiled for an hour in a flask fitted with a vertical condenser, neutralised while hot with precipitated chalk, filtered, and evaporated at 60° down to a syrupy consistency. It is then precipitated with alcohol, and the alcoholic liquid evaporated down to the condition of an extract, but no trace of any crystals appeared even after twelve days; ether was therefore added to the alcoholic solution, and from the ethereal solution crystals of arabinose were obtained after partial evaporation.

A General Method for the Preparation of the Mixed Carbonic Ethers of the Fatty and Aromatic Series.—P. Cazeneuve and A. Morel.—Will be inserted in full.

NOTES AND QUERIES.

*** Our Notes and Queries column was opened for the purpose of giving and obtaining information likely to be of use to our readers generally. We cannot undertake to let this column be the means of transmitting merely private information, or such trade notices as should legitimately come in the advertisement columns.

Estimation of Zinc and Lead.—Will any of your readers kindly give me any information on the estimation of (1) zinc from 2 to 7 per cent, and (2) lead from ½ to 5 per cent, in slags and mattes containing large quantities of iron and lime? The methods should be rapid and fairly accurate.—Cox.

MEETINGS FOR THE WEEK.

Wednesday, 11th.—Society of Arts, 7. (Juvenile Lecture). "Some Ways in which Animals Breathe," by Prof. F. Jeffrey Bell.

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Manuals: E. Chr. Hansen, "Practical Studies in Fermentation," London (Spon), 1896). Alfred Jörgensen, "Micro-Organisms and Fermentation," London (F. W. Lyon), 1893.

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This issue of the Chemical News contains a Supplement devoted to—

A TABULAR ATLAS

OF THE

CHEMISTRY OF THE METALS,

Cs, Rb, and K.

which, it is hoped, will impart a tolerably satisfactory idea of the plan of the work, and the opinions of Eminent Scientists and the Chemical Press concerning it.

In the small fragment given as a specimen of its pages (one-half of one page, and that made up of selections from others), examples of *many divisions* of the "Atlas," and numerous footnotes containing *references to original sources*, are necessarily omitted on account of *deficient space*.

Tabulated Quantitative Analysis, occupying 18 or 20 pages in columnar form, with catch-line headings, could not, therefore, be exhibited.

In that great division, hundreds of methods receive extended consideration; it is arranged in three sub-sections:—

1. Determination of the Element.—Here we find methods (in the case of K) for estimating the metal as $KClO_4$, KCl, K_2PtCl_6, K_2CO_3, K_2SiF_6, KNO_3, K_2SO_4, Bismuth-thiosulphate, KHT, indirectly, spectroscopically, and volumetrically, &c.

2. Analysis of Natural or Technical Products.—Schemes for analysing KBr, $KClO_3$, KCl, KCN, Ferro-, Ferri-, and Sulpho-cyanides, KHO, the Carbonates, and Tartrates; commercial Sulphates, Muriates, &c.; Fertilisers, Plant Ashes, &c.; for the breaking-up of Silicates (two dozen methods); and for the Toxicological Detection of Poisons.

3. Separation from Other Elements.—In all cases the arrangement is as follows:—(*a*). Name of form of combination in which the metal is isolated. (*b*). Variations of the method. (*c*). Brief abstract of plan of procedure. (*d*). Detailed instructions. (*e*). Name of author of method and the reference. (*f*). Comments of chemists on the method, and original experiments.

Toxicology, Metallurgy, and Manufacture also find no place in the specimen; they extend over many pages, presenting features the reader will in vain seek for elsewhere.

On application to the author, a two-page selection of excerpts from the work, containing the explanatory introduction, and accompanied by descriptive circulars, will be forwarded free.

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UNIVERSITY OF ST. ANDREWS.

The University Court of St. Andrews will, at a meeting to be held on January 24, 1899, appoint, for a period of two years as from January 1, 1899, an ADDITIONAL EXAMINER for Graduation in the subject of Chemistry.

Further information may be obtained from Mr. C. S. Grace, W.S., Secretary of the University Court, with whom applications, with testimonials, may be lodged until 14th prox.

St. Andrews, December, 1898.

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THE CHEMICAL NEWS.

Vol. LXXIX., No. 2042.

NOTE ON THE

DENSITIES OF "ATMOSPHERIC NITROGEN," PURE NITROGEN, AND ARGON.*

By WILLIAM RAMSAY, F.R.S.

M. A. Leduc, in a recent paper ("Recherches sur les Gaz," *Ann. Chim. Phys.*, September, 1898), has discussed the relation between the density of argon, its proportion in atmospheric nitrogen, the density of the latter, and that of pure nitrogen. It appears to me that he has misunderstood some of the data given by Lord Rayleigh, Dr. Kellas, and myself; and as the question whether the found density of argon corresponds with that calculable from the other data, is in itself an interesting one, I have the honour to present this note to the Society.

The data may be divided into two groups, those of Leduc and Schloesing; and those of Rayleigh, Ramsay, and Kellas.

From the first group it is possible to calculate the density of argon, *i.e.*, the crude mixture left after separating oxygen and nitrogen from air.

From the second group the density of argon may be calculated; or if that be assumed, both groups give data for the calculation of that of "atmospheric" nitrogen. It has been thought better to express the results in the form of the weight of one litre of the gas in question; but if it is desired to state them with reference to the density of oxygen = 16, the conversion may be made by means of the weight of a litre of oxygen according to both Lord Rayleigh and M. Leduc.

The data are as follows:—

Weight of 1 litre of	Leduc.	Rayleigh.	Schloesing.	Kellas.	Ramsay.
Air	1·29316	1·29327			
Oxygen	1·42920	1·42952			
Nitrogen ..	1·25070	1·25092			
„ (atmo.)	1·25700	1·25718			
Argon	—	1·78151	—	—	1·7816
„ in "atmo." nitrogen..	—	—	0·01183	0·01186	

Weight of 1 litre argon calculated from Leduc's and Schloesing's figures:—

$0{\cdot}01183x = 1{\cdot}25700 - (1{\cdot}25070 \times 0{\cdot}98817)$; hence $x = 1{\cdot}7828$.

The difference from the value found is 7 in 10,000.

Weight of 1 litre argon calculated from Rayleigh's and Kellas's figures:—

$0{\cdot}01186x = 1{\cdot}25718 - (1{\cdot}25092 \times 0{\cdot}98814)$; hence $x = 1{\cdot}7791$.

The difference from the value found is 13 in 10,000.

Both of these results are quite satisfactory, considering that the nature of the calculation involves a ratio of small differences. The agreement is more striking if the density of "atmospheric" nitrogen is calculated from the figures; for this calculation the weight of 1 litre of argon is assumed to be 1·7815 grms.

Weight of 1 litre of "atmospheric" nitrogen from Leduc's and Schloesing's figures:—

$x = (1{\cdot}7815 \times 0{\cdot}01183) + (1{\cdot}25070 \times 0{\cdot}98817)$; whence $x = 1{\cdot}25698$.

Here the difference is only 2 in 125,000.

From Lord Rayleigh's and Dr. Kellas's figures, we have:—

$x = (1{\cdot}7815 \times 0{\cdot}01186) + (1{\cdot}25092 \times 0{\cdot}98814)$; whence $x = 1{\cdot}25721$.

The difference here is only 3 in 125,000.

It is thus evident that either set of figures gives results as concordant as could be wished; and that the density of "atmospheric" nitrogen is correctly given as the mean of the densities of the constituents, taken in the proportion in which they occur.

* A Paper read before the Royal Society, December 15, 1898.

THE

SPECTRUM OF A RADIO-ACTIVE SUBSTANCE.

By EUG. DEMARCAY.

M. and Mdme. Curie have asked me to examine, spectroscopically, a substance consisting chiefly of barium chloride, but supposed by them to contain also a new element. The material was dissolved in distilled water, slightly acidulated with hydrochloric acid. The spark spectrum of this solution was very brilliant. I photographed the spectrum, having prepared two plates, and giving one double the time of exposure of the other. These two plates gave practically identical results. I measured the lines, and was able to see:—(1) Barium, with great intensity of both the strong and weak lines; (2) lead, recognised by its principal lines, which were much more feeble than the others; (3) platinum, due to the electrodes and traces of calcium probably from the solvent; (4) a line, stronger than the weak lines of barium, with wave length 3814·8 (Rowland's scale). This line does not appear to have been attributed to any known element, and is probably due to a new substance, for two reasons. Firstly, that on the plate were no lines, other than these enumerated, except a few feeble air lines, thus excluding the presence of all elements having only weak lines in the neighbourhood of 3814. Secondly, the methods employed for the purification of the substance prevent the possibility of the presence of iron, chromium, cobalt, or nickel, &c. Barium and lead, I am fully assured, give no line coinciding with this.

This line has been measured by means of the two platinum lines, 3818·9 and 3801·5, which enclose it. It is near to and distinct from a bismuth line of moderate intensity.

Conclusion.—The presence of the line 3814·8 confirms the existence of a small quantity of a new element in M. and Mdme. Curie's barium chloride.—*Comptes Rendus*, cxxvii., No. 26.

A COLORIMETRIC METHOD FOR THE ESTIMATION OF SILICA IN WATER.

By A. JOLLES and F. NEURATH.

As is well known, the silica contained in water in the form of hydrated silicic acid, or of an alkaline silicate, is estimated by being transformed into insoluble silica. Although, as a rule, we take no account of the presence of silica in potable water, or in water used for boilers, a simple and rapid method for estimating silica in water might be of service, if only for determining to what point different sorts of glass are attacked by water.

This method enables us to rapidly estimate small quantities of silica, and may be effected on very small quantities of liquid. We know that the alkaline molybdates give with silica in the presence of free nitric acid complex yellow compounds, similar to those which they form with phosphoric and arsenic acids. Among the alkaline silico-molybdates, the silico-molybdate of potassium is the most soluble, and in aqueous solution has a pronounced yellow colour, the intensity of which increases with the temperature, attaining its maximum towards 70° or 80°. This coloured reaction can be utilised for the approximate estimation of silica in water,

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For this purpose we use a solution of molybdate of potassium, prepared by dissolving 8 grms. of this salt in 50 cubic c.m. of water, and adding 50 cubic c.m. of pure nitric acid of 1·2 density. We pour 20 cubic c.m. of the water to be examined into a narrow test-tube—the water should stand about 18 c.m. high; we add 1 cubic c.m. of the molybdic solution, and notice the colour obtained. As a colorimetric scale we use a series of test-tubes as near as possible of the same form and dimensions as the first, each containing 20 cubic c.m. of pure distilled water, to which has been added a known quantity of silicate of soda and 1 cubic c.m. of the molybdic solution. All these test-tubes are heated together to 80°. We then compare the colour produced by the water under examination with the colorimetric scale, and thus determine approximately the proportion of silica in the water.

The possible presence of phosphoric or arsenic acid in the water might have some influence on the colouration obtained, and consequently on the result of the analysis. But, generally speaking, the quantity of phosphoric acid present in a natural water is so slight that it can only be detected after concentrating the liquid. As to arsenic acid it is practically never found in natural waters.

However, we might evaporate the sample down with nitric acid several times, separate the silica by filtration, add water to the filtrate, so as to make it up to its original volume, and repeat the colorimetric test on 20 cubic c.m. of this solution. If no yellow colouration is obtained, the absence of both phosphoric and arsenic acids may be considered proved. In the contrary case it must be taken account of in the final calculation.

To verify the exactness of this method we estimated the silica in a number of samples, both by the colorimetric method and by the usual gravimetric method. The results obtained were satisfactory.—*Zeit. für. Augewandte Chemie*, 1898, p. 315.

ON THE

ANALYSIS OF MOLYBDENUM COMPOUNDS.

By HARRY BREARLEY.

(Concluded from p. 5).

The Estimation of Phosphorus.

For various reasons it has become common, after having separated phosphorus as ammonium phospho-molybdate, to proceed to estimate some other constituent of the precipitate, — the volumetric estimation of the reduced molybdenum with permanganate, for instance. It appears as though the molybdenum might easily be estimated gravimetrically by the above process. The operation is certainly not hampered by any such uncertainty as to whether Mo_2O_3, Mo_8O_{13}, or $Mo_{12}O_{19}$, is the state to which the molybdenum is reduced. A further examination will show what the relative advantages of the gravimetric process are.

PS.—The interferences of a very important element—tungsten—is conspicuously absent. It has not been overlooked.

Appendix.

The Estimation of Lead as Molybdate.

In the paper by Chatard (Chemical News, xxiv., 175), previously referred to, he says "I tried to determine lead as molybdate, but without success, as the presence of an excess of the precipitant seems to exert an injurious effect, the filtrate or washings speedily becoming cloudy."

The fact that molybdate of lead is exceptionally insoluble in the solutions from which it may be precipitated, that the ratio Pb : $PbMoO_4$ is lower than the corresponding ratio for either the sulphate or chromate of lead, and that the precipitate may be safely ignited along with the paper, are good reasons for seeking to obviate the difficulty Chatard alludes to.

We have already remarked that, in presence of an excess of lead acetate, the most easily filtrable form of the precipitated lead molybdate is obtained by decomposing the hydrochloric acid, which is keeping the $PbMoO_4$ dissolved, by means of ammonium acetate. If a like procedure be followed in presence of an excess of sodium (or ammonium) molybdate, the lead comes down as a lustrous silky precipitate, somewhat resembling the well-known precipitation of manganese as ammonium manganese phosphate. This precipitate can be filtered and washed with the greatest ease.

The following differences may also be noticed. If an excess of molybdate be added to a solution of lead acidified with HCl only so far as to prevent a precipitate being formed in the cold, then, on warming, the precipitate forms. With an excess of lead acetate the reverse is the case.

The colour of the lead molybdate is more creamy than when precipitated with an excess of lead acetate.

In a series of test analyses the lead acetate used was a commercial sample, and therefore not quite trustworthy as to purity. In order to be assured that the precipitate finally obtained was really pure $PbMoO_4$ it was redissolved in HCl and re-precipitated with an excess of lead acetate. In every case the second result was higher than the first, and pointed to an error which was afterwards found to be inseparable from the use of "acid precipitation" with an excess of molybdate, viz., the contamination of lead molybdate with molybdic acid. The extent of this error may be sufficiently shown by two examples in which an excess of 20 to 30 per cent of precipitant was used.

Grms. lead added.	Lead found.	Error.
0·2284	0·2308	0·0024
0·0914	0·0925	0·0011

This error decreases with the excess of molybdate used, so that, if the precipitate be re-dissolved in hydrochloric acid and re-precipitated with ammonium acetate without any further addition of either $(NH_4)_2MoO_4$, or PbA_2, the ideal conditions are almost attained and the results are very accurate.

An equally accurate result is obtainable by re-precipitating with an excess of lead acetate, and calculating the difference between the first and second weights of $PbMoO_4$ into MoO_3, and subtracting the number found from the first weight. Thus an actual example gave—

Weight of first precipitate of $PbMoO_4$		0·4093 grm.
,, second ,,	,,	0·4210 ,,
		0·0117 ,,

0·0117 $PbMoO_4$ = 0·0046 MoO_3.

0·4093 − 0·0046 = 0·4047 grm. of lead molydate, instead of 0·4051 grm. which it should weigh theoretically.

The acid precipitation is set forth at such length because here, as in the converse case, it is especially valuable where lead is being estimated, without previous separation, in a great number of its combinations and alloys with other metals.

Chatard's form of precipitation was now repeated, in order to see if a compact pulp filter could overcome the difficulty he mentions. The filtered and unfiltered portions were hardly distinguishable from each other, and, like those unfiltrable clayey waters, prolonged standing showed no appreciable settling. But this difficulty is due altogether to the fact that the experiment was made, both in Chatard's case and my own, with practically pure materials. On adding ammonium chloride to the unfiltrable solution the precipitate agglomerates, and on digesting becomes granular and easily filtrable. For pure solutions, then, and probably in the presence of such elements as have been shown not to interfere with the converse opera-

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tion carried out in the ordinary way, it is simply necessary to add ammonium chloride either before or along with the excess of the alkaline molybdate. The lead separates as pure $PbMoO_4$, and re-precipitation is unnecessary.

Test Analyses.

Lead added.	Lead found.	Error.
0.3198	0·3200	0·0002
0·2284	0·2285	0·0001
0·1371	0·1370	0·0001
0·0914	0·0914	0·0000
0·0457	0·0457	0·0000
0·0229	0·0231	0·0002

Totley, near Sheffield.

DERIVATIVES OF THE TETRACHLORIDES OF ZIRCONIUM, THORIUM, AND LEAD.*

By J. MERRITT MATTHEWS.

(Continued from p. 7).

4. Action of Fatty and Aromatic Amines.

It was in this field that positive results were at last encountered. Silicon, titanium, and tin tetrachlorides all give compounds with the amines, and analogy would lead us to expect that the chlorides here used would behave in a similar manner, as indeed was the case. These derivatives with the amine bases, including ammonia, are apparently peculiar additive products, showing that these tetrachlorides, in common with the other chlorides of this group, possess an acid character.

The compounds herein described were obtained by the simple addition of the pure anhydrous reagents to the solutions of the respective tetrachlorides. The zirconium and thorium derivatives, for the most part, were white flocculent precipitates; the lead salts, however, gave compounds of various colours.

The analysis of these derivatives was carried out in the following manner:—With the zirconium and thorium compound a weighed quantity was placed in a small beaker-glass and covered with nitric acid containing a solution of silver nitrate, and gently warmed. This sufficed to decompose the substance, the chlorine present being precipitated as silver chloride. The liquid was diluted with water, the chloride filtered off, and from its weight the chlorine was estimated. Excess of ammonia water was added to the filtrate, and the resulting precipitate of zirconium or thorium hydroxide was filtered off and ignited to the corresponding dioxide, from the weight of which the zirconium or thorium was estimated. The nitrogen present in the ammonia derivatives was determined by heating a portion with a strong solution of sodium hydroxide, and passing the evolved ammonia into a standardised solution of hydrochloric acid, and either titrating the excess of acid with standard alkali, or precipitating the ammonia in the usual manner with a solution of platinic chloride, and from the weight of the platinum left after ignition calculating the quantity of nitrogen. With the amine derivatives the Kjeldahl method was employed; and the Will and Varrentrap method was used for the quinoline and pyridine compounds. The lead compounds were decomposed with warm nitric acid, and the lead determined as sulphate by evaporation with sulphuric acid in the usual manner, the chlorine being determined by heating the compound with sulphuric acid in a distilling flask, passing the evolved hydrochloric acid gas into a solution of silver nitrate, and weighing the silver chloride as usual. The nitrogen present was estimated as with the zirconium and thorium derivatives.

* Contribution from the John Harrison Laboratory of Chemistry. From the *Journal of the American Chemical Society*, xx., No. 11. From author's thesis for the Degree of Doctor of Philosophy.

A. *Ammonia.*

Paykull (*Ber. d. Chem. Ges.*, vi., 1467) obtained a compound of zirconium tetrachloride with ammonia by heating the former with NH_4Cl, and to this compound he ascribes the formula $ZrCl_4{\cdot}4NH_3$. Besson (*Compt. Rend.*, cx., 240) has also obtained an ammonia derivative with silicon tetrachloride, giving it the formula $SiCl_4{\cdot}6NH_3$. With tin tetrachloride Rose (*Pogg. Ann.*, xx., 147) obtained the compound $SnCl_4{\cdot}4NH_3$, though Persoz (*Ann. Chim. Phys.*, xlvi., 305) claims to have made $SnCl_4{\cdot}6NH_3$. With titanium tetrachloride Rose (*Pogg. Ann.*, xx., 147) obtained the compound $TiCl_4{\cdot}4NH_3$, though Persoz (*vide supra*) gives the formula as $TiCl_4{\cdot}6NH_3$.

a. Zirconium Tetrachloride, $ZrCl_4{\cdot}8NH_3$.—On passing dry ammonia gas into the solution of zirconium tetrachloride, a white flocculent precipitate was immediately produced, with considerable evolution of heat. This compound on drying appeared to be stable in the air, though on gently heating it gave off fumes of ammonium chloride. Its analysis showed the presence of eight molecules of ammonia.

I. 0·5625 grm. material gave:—

0·8729 grm. silver chloride = 0·2161 grm. chlorine = 38·42 per cent chlorine.

0·1860 grm. zirconium dioxide = 0·1374 grm. zirconium = 24·44 per cent zirconium.

II. 0·1862 grm. material gave:—

0·2881 grm. silver chloride = 0·0713 grm. chlorine = 38·30 per cent chlorine.

0·0623 grm. zirconium dioxide = 0·0460 grm. zirconium = 24·71 per cent zirconium.

0·0624 grm. material gave 0·0228 grm. ammonia = 36·60 per cent ammonia.

0·5625 grm. material gave 0·2084 grm. ammonia = 37·05 per cent ammonia.

	Calculated for $ZrCl_4{\cdot}8NH_3$.	Found. I.	Found. II.
Chlorine	38·52	38·42	38·30
Zirconium	23·58	24·44	24·71
Ammonia	36·90	36·60	37·05

$ZrCl_4{\cdot}2NH_3$.—On passing dry ammonia gas over the solid zirconium tetrachloride contained in a porcelain boat, a considerable evolution of heat was observed, evidently showing that combination resulted. The compound thus obtained was white in colour, fumed in the air, and rapidly took up moisture, rendering it difficult to analyse with accuracy.

0·5304 grm. zirconium tetrachloride, after being treated with ammonia gas for two hours, on re-weighing gave 0·6247 grm.

This on analysis gave:—

1·3778 grm. silver chloride = 0·3163 grm. chlorine = 50·67 per cent chlorine.

0·2927 grm. zirconium dioxide = 0·2163 grm. zirconium = 34·62 per cent zirconium.

	Calculated for $ZrCl_4{\cdot}2NH_3$.	Found.
Chlorine	51·81	50·67
Zirconium	33·21	34·26
	Grm.	Grm.
Increase in weight	0·0917	0·0943

$ZrCl_4{\cdot}4NH_3$.—On heating zirconium tetrachloride in a current of dry ammonia gas, a compound was obtained which was white in colour, and unstable on exposure to the air.

0·4713 grm. zirconium tetrachloride being gently heated (to about 100° C.) in ammonia gas, on re-weighing gave 0·6123 grm.

This on analysis gave:—

1·1397 grm. silver chloride = 0·2821 grm. chlorine = 46·07 per cent chlorine.

0·2588 grm. zirconium dioxide = 0·1912 grm. zirconium = 31·23 per cent zirconium.

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	Calculated for $ZrCl_4 \cdot 4NH_3$.	Found.
Chlorine	47·24	46·07
Zirconium	30·14	31·23
	Grm.	Grm.
Increase in weight	0·1378	0·1410

These results seem to indicate that zirconium tetrachloride may be combined with ammonia in three proportions, depending upon the conditions under which the combination is brought about. When in ethereal solution it takes up eight molecules of ammonia, giving $ZrCl_4 \cdot 8NH_3$; the dry salt unaided by heat gives $ZrCl_4 \cdot 2NH_3$; and with the aid of heat the latter also gives the compound $ZrCl_4 \cdot 4NH_3$. All of these bodies are white in colour, the first one only being stable in the air. The last of the above derivatives seems to be identical with the one obtained by Paykull.

b. Thorium Tetrachloride.—As the field of thorium derivatives has not been investigated in any very exhaustive manner, one would not be likely to encounter any preceding research in the rather remote class of compounds herein dealt with. Chydenius (*Jsb. Chem.*, 1863, 194), however, has prepared a derivative of thorium tetrachloride with ammonium chloride, to which he has given the formula $ThCl_4 \cdot 8NH_4Cl$. It is of interest to note that the compound prepared in this present research also contains the same molecular proportions of ammonia to thorium.

$ThCl_4 \cdot 8NH_3$.—Dry ammonia gas passed into the solution of thorium tetrachloride produced a white flocculent precipitate, which, on drying, continued stable in the air. On heating it decomposed with the evolution of fumes of ammonium chloride.

I. 0·5870 grm. material gave :—

0·6526 grm. silver chloride = 0·1616 grm. chlorine = 27·52 per cent chlorine.

0·3054 grm. thorium dioxide = 0·2684 grm. thorium = 45·73 per cent thorium.

II. 0·6212 grm. material gave :—

0·5928 grm. silver chloride = 0·1715 grm. chlorine = 27 61 per cent chlorine.

0·3212 grm. thorium dioxide = 0·2824 grm. thorium = 45·46 per cent thorium.

0·5172 grm. material gave 0·1366 grm. ammonia = 26·41 per cent ammonia.

	Calculated for $ThCl_4 \cdot 8NH_3$.	Found. I.	Found. II.
Chlorine	27·80	27·52	27·61
Thorium	45·55	45·73	45·46
Ammonia	26·64	26·41	—

$ThCl_4 \cdot 6NH_3$.—On allowing dry ammonia gas to pass over a portion of thorium tetrachloride placed in a porcelain boat, a considerable evolution of heat was observed, the ammonia evidently reacting with the salt. The resulting compound was white in colour, and fumed in moist air, though it appeared to be more stable than the corresponding zirconium derivative obtained under the same conditions.

0·4217 grm. material, on being treated with ammonia gas for two hours, on re-weighing gave 0·5352 grm. This on analysis gave :—

0·6274 grm. silver chloride = 0·1553 grm. chlorine = 29·01 per cent chlorine.

0·3021 grm. thorium dioxide = 0·2656 grm. thorium = 49·62 per cent thorium.

	Calculated for $ThCl_4 \cdot 6NH_3$.	Found.
Chlorine	29·79	29·01
Thorium	48·80	49·62
	Grm.	Grm.
Increase in weight	0·1148	0·1135

On gently heating thorium tetrachloride to about 100° C. in a current of ammonia gas, a compound was obtained identical with the one just described above; it possessed the same appearance, and analysed for the same formula. At a higher temperature decomposition seemed to take place, and copious fumes of ammonium chloride were formed.

c. Lead Tetrachloride, $PbCl_4 \cdot 4NH_3$.—On treating the chloroform solution of lead tetrachloride with dry ammonia gas, an orange-yellow precipitate was at first produced, which rapidly became white in colour as more ammonia was absorbed. A great amount of heat was evolved in the reaction, and the compound continued stable in the air.

I. 0·3600 grm. material gave :—

0·2597 grm. lead sulphate = 0·1774 grm. lead = 49·30 per cent lead.

0·2614 grm. material gave :—

0·3205 grm. silver chloride = 0·0816 grm. chlorine = 33·76 per cent chlorine.

II. 0·2582 grm. material gave :—

0·1874 grm. lead sulphate = 0·1281 grm. lead = 49·62 per cent lead.

0·2075 grm. material gave :—

0·2844 grm. silver chloride = 0·0704 grm. chlorine = 33·92 per cent chlorine.

0·4201 grm. material gave :—

0·3817 grm. platinum = 0·0664 grm. ammonia = 15·81 per cent ammonia.

	Calculated for $PbCl_4 \cdot 4NH_3$.	Found. I.	Found. II.
Lead	49·88	49·30	49·62
Chlorine	34·05	33·76	33·92
Ammonia	16·07	15·81	—

$PbCl_4 \cdot 2NH_3$.—By using a more concentrated solution of lead tetrachloride, and interrupting the treatment with ammonia gas before all of the lead salt was neutralised, an orange-yellow precipitate was obtained. This fumed in the air and decomposed on standing. Its analysis indicated the above formula.

0·3017 grm. material gave :—

0·2375 grm. lead sulphate = 0·1622 grm. lead = 53·75 per cent lead.

0·2332 grm. material gave :—

0·3525 grm. silver chloride = 0·0873 grm. chlorine = 37·42 per cent chlorine.

0·2716 grm. material gave :—

0·1430 grm. platinum = 0·0249 grm. ammonia = 9·16 per cent ammonia.

	Calculated for $PbCl_4 \cdot 2NH_3$.	Found.
Lead	54·16	53·75
Chlorine	37·00	37·42
Ammonia	8·85	9·16

B. *Methylamine.*

a. Zirconium Tetrachloride, $ZrCl_4 \cdot 4CH_3NH_2$.—On conducting the vapours of methylamine into the solution of zirconium tetrachloride, a white flocculent precipitate was formed. Analysis showed that it followed the same general type as the other derivatives.

I. 0·2417 grm. material gave :—

0·3833 grm. silver chloride = 0·0949 grm. chlorine = 39·26 per cent chlorine.

0·0838 grm. zirconium dioxide = 0·0619 grm. zirconium = 25·62 per cent zirconium.

II. 0·5432 grm. material gave :—

0·8674 grm. silver chloride = 0·2147 grm. chlorine = 39·53 per cent chlorine.

0·1786 grm. zirconium dioxide = 0·1339 grm. zirconium = 25·65 per cent zirconium.

0·6021 grm. material gave :—

0·1165 grm. ammonia = 0·0969 grm. nitrogen = 15·95 per cent nitrogen.

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	Calculated for $ZrCl_4 \cdot 4CH_3NH_2$.	Found. I.	Found. II.
Chlorine	39·82	39·36	39·53
Zirconium ..	25·41	25·62	25·65
Nitrogen	16·18	15·95	—

b. Thorium Tetrachloride, $ThCl_4 \cdot 4CH_3NH_2$.—The compound obtained with thorium tetrachloride showed the presence of four molecules of the base. Indeed this seems to be the general type after which all these derivatives are modelled.

0·6513 grm. material gave:—
0·7451 grm. silver chloride = 0·1802 grm. chlorine = 28·32 per cent chlorine.
0·3461 grm. thorium dioxide = 0·3040 grm. thorium = 46·71 per cent thorium.
0·5318 grm. material gave:—
0·0712 grm. ammonia = 0·0587 grm. nitrogen = 11·03 per cent nitrogen.

	Calculated for $ThCl_4 \cdot 4CH_3NH_2$.	Found.
Chlorine	28·48	28·32
Thorium	46·65	46·71
Nitrogen	11·24	11·03

c. Lead Tetrachloride, $PbCl_4 \cdot 4CH_3NH_2$.—The compound obtained with lead tetrachloride was also white in colour, and stable in the air. Analysis proved it to be analogous to the preceding derivatives.

0·2506 grm. material gave:—
0·2969 grm. silver chloride = 0·0735 grm. chlorine = 29·32 per cent chlorine.
0·2716 grm. material gave:—
0·1757 grm. lead sulphate = 0·1200 grm. lead = 44·17 per cent lead.
0·2517 grm. material gave:—
0·2005 grm. platinum = 0·0289 grm. nitrogen = 11·42 per cent nitrogen.

	Calculated for $PbCl_4 \cdot 4CH_3NH_2$.	Found.
Chlorine	30·02	29·32
Lead	43·76	44·17
Nitrogen	11·84	11·42

C. *Ethylamine.*

a. Zirconium Tetrachloride, $ZrCl_4 \cdot 4C_2H_5NH_2$.—As would be expected from its behaviour with the preceding amine, zirconium tetrachloride was found to yield a derivative with ethylamine.

0·5418 grm. material gave:—
0·7478 grm. silver chloride = 0·1856 grm. chlorine = 34·26 per cent chlorine.
0·1619 grm. zirconium dioxide = 0·1196 grm. zirconium = 22·08 per cent zirconium.
0·6516 grm. material gave:—
0·0861 grm. ammonia = 0·0709 grm. nitrogen = 10·89 per cent nitrogen.

	Calculated for $ZrCl_4 \cdot 4C_2H_5NH_2$.	Found.
Chlorine	34·42	34·26
Zirconium	21·96	22·08
Nitrogen	10·79	10·89

b. Thorium Tetrachloride, $ThCl_4 \cdot 4C_2H_5NH_2$.—Ethylamine gave a white compound with thorium tetrachloride.

0·2102 grm. material gave:—
0·2137 grm. silver chloride = 0·0528 grm. chlorine = 25·12 per cent chlorine.
0·0995 grm. thorium dioxide = 0·0874 grm. thorium = 41·58 per cent thorium.
0·5912 grm. material gave:—
0·0712 grm. ammonia = 0·0587 grm. nitrogen = 9·92 per cent nitrogen.

	Calculated for $ThCl_4 \cdot 4C_2H_5NH_2$.	Found.
Chlorine	25·60	25·12
Thorium	41·94	41·58
Nitrogen	10·10	9·92

c. Lead Tetrachloride, $PbCl_4 \cdot 4C_2H_5NH_2$.—Ethylamine gave at first a yellow precipitate with the solution of lead tetrachloride, which went over to a white compound on the addition of more ethylamine.

0·2072 grm. material gave:—
0·2220 grm. silver chloride = 0·0550 grm. chlorine = 25·52 per cent chlorine.
0·2506 grm. material gave:—
0·1459 grm. lead sulphate = 0·0996 grm. lead = 39·76 per cent lead.
0·3817 grm. material gave:—
0·2746 grm. platinum = 0·0394 grm. nitrogen = 10·32 per cent nitrogen.

	Calculated for $PbCl_4 \cdot 4C_2H_5NH_2$.	Found.
Chlorine	26·84	26·52
Lead	39·13	39·76
Nitrogen	10·59	10·32

(To be continued).

CERTAIN ALKALOIDAL PERIODIDES, AND THE VOLUMETRIC ESTIMATION OF ALKALOIDS AS HIGHER PERIODIDES.*

By A. B. PRESCOTT and H. M. GORDIN.†

The Periodides in Respect to Completeness of Precipitation.

In aqueous solutions of salts of the alkaloids, one of the most delicate of qualitative reagents is iodopotassium iodide. Wormley gives the limit of this precipitation, for the chief medicinal alkaloids, as from $\frac{1}{250000}$ to $\frac{1}{2500000}$ of a grain of the alkaloid in one grain of water; that is, from 0·0000013 to 0·0000007 grm. in 1 c.c. of water ("Microchemistry of Poisons," 1885, Tabular View). The precipitate is not appreciably soluble in excess of the reagent, an advantage over several other qualitative precipitations of alkaloids in general. In some cases the precipitate is appreciably soluble in excess of the alkaloidal salt, and this condition is one most easy to avoid. The potassium iodide solution of iodine was recommended as a reagent for alkaloids by Bouchardat, a medical writer in Paris, in 1839 (Bouchardat, 1839, *Compt. Rend.*, ix., 475; *L'Institut*, vii., 358). This precipitation, however, was proposed as an antidote for strychnine, in cases of poisoning of dogs. Further, see Donné (*Ann. Chim. Phys.* (2), xxxviii., 82).

As a volumetric solution, the decinormal solution of iodine with potassium iodide was first proposed by Wagner, in 1861 (R. Wagner, Dingler's *Poly. J.*, clxi., 40; *Ztschr. Anal. Chem.*, i., 102), and the decinormal strength is generally the most suitable for volumetric use.

Historical as to the Formation of Perhalides in General.

The formation of the alkaloidal periodides was first made a subject of systematic observation by Jörgensen, at Copenhagen, in 1869 (Jörgensen, 1869-1878, *J. Prakt. Chem.* (2), ii., 347, 433; iii., 145, 328; xiv., 213, 356; xv., 65, 418; xvi., 352; *Ber. d. Chem. Ges.*, ii., 460), and the masterly researches of this Danish chemist, extending over nine years, afford a model of logical inquiry into chemical structure. A still wider study of all periodides and some other perhalides of organic bases was commenced in 1887 by Professor Geuther (A. Geuther, *Ann. Chem. Pharm.* (Liebig), ccxl., 66·91, with lists of the

* The portion of this article which concerns atropine was given in substance in the *Journ. Am. Chem. Soc.*, xx., 329, under the title, "Atropine Periodides and Iodomercurates," by H. M. Gordin and A. B. Prescott (reprints). Also that concerning morphine and opium, except the "Results of Opium Assay," appeared in Kremers' *Pharmaceutical Archives*, June, 1898, i., 121, under the title, "A Volumetric Assay of Opium," by H. M. Gordin and A. B. Prescott (reprints).

† In the work of Research Committee D, Section 2, Committee on Revision of the Pharmacopœia of the United States.

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organic periodides previously obtained), of Jena, but was cut short by his death in 1889. Among various periodides reported of later years have been picoline periodides by William Ramsay in 1878 (*Phil. Mag.* (5), ii., 269; iv., 241; vi., 19); cæsium and rubidium periodides by Wells, and others in 1893 (*Am. J. Sci.* (3), xliv., 42; xliii., 17); iodonium periodides by Victor Meyer in 1894 (*Ber. d. Chem. Ges.*, xxvii., 1594); sulphon periodides by Kastle in 1894 (*Am. Chem. J.*, xvi., 116); periodides of diazo bodies by Hantsch in 1895 (*Ber. d. Chem. Ges.*, xxviii., 2754); halogen addition-products of the anilides by Wheeler and others in 1896-97 (*Am. Chem. J.*, xviii., 85; xix., 672); perhalides of aliphatic amines by Norris in 1898 (*Am. Chem. J.*, xx., 51); mixed perhalides of alkyl anilines by Samtleben in 1898 (A. Samtleben, *Ber. d. Chem. Ges.*, xxxi., 1141).

In this laboratory since 1895 the perhalides and various double halides of pyridine have been obtained,* also the perhalides of caffeine (Gomberg, Perhalides of Caffeine, *Journ. Amer. Chem. Soc.*, xviii., 347-378), and work on picoline perhalides is in hand. In the course of work upon an entirely different inquiry, a new order of perhalides has just been obtained, a periodide of brom-triphenylmethane.†

It is of interest to inquire what classes of compounds are liable to the formation of perhalides, and this inquiry has a special interest when it is proposed to estimate a single class of compounds, in vegetable drugs or their extracts, by formation of periodide. In general terms the reply is easily given, that periodides are limited to the organic basis, that is the more or less basal compounds of the nitrogen family of elements, and the inorganic alkalies. It is remarkable that the iodonium compounds yield periodides, which is quite in accord with the claim of Victor Meyer that in these bodies iodine itself strangely serves (with the benzene ring) as a base-forming element like a member of the nitrogen family. This view is supported further by Gomberg's production at this time of a periodide of a triphenylmethane derivative, as cited just above.

At present it seems highly improbable that any plant constituent other than the alkaloids, in the larger sense of organic bases, are of the sort of bodies which can form periodides in precipitation. Moreover, Wagner's reagent is used in a qualitative way along with plant analysis to an extent likely to call attention to any interference with its use for alkaloids. From the work of Wheeler it is evident that periodides may be formed by acid amides, but probably not by precipitation in dilute solutions. The formation of iodonium periodides, and a sulphone periodide, indicate that the limits of formation of perhalides cannot yet be declared, and it will be well for analysts to be watchful of new developments.

Historical as to Analytical Use of Periodides.

The volumetric use of a potassium iodide aqueous solution of iodine dates from Wagner in 1861, and the solution in decinormal strength of iodine is named Wagner's reagent.

(Note.—R. Wagner, 1861, *Ding. Poly. J.*, clxi., 40; *Ztschr. Anal. Chem.*, i., 102. Wagner wisely avoided washing the precipitate, but he failed to add the solution of alkaloid to that of iodine:—"Man versetzt die Losung der Basen, deren Menge man bestimmen will, mit überschüssiger Iod lösung, filtrirt und bestimmt in einem gemessenen Theil des Filtrats mit unterschwefligsaurem Natron das überschüssige Iod." As periodides had not then been prepared and analysed, the iodine factors of Wagner were empirical, and, as the higher periodides are not invariably the sole products when iodine solution *is added to* the alkaloid solution, the factors adopted proved unsatisfactory. It is noteworthy that "Mayer's reagent" was so nearly contemporaneous with Wagner's in publication. The potassium mercuric iodide method of volumetric estimation dates from 1862—*Proc. Am. Pharm. Assoc.*, 230; *Am. J. Pharm.*, xxxv., 20; Chemical News, vii., 159; viii., 177, 189. Of special American interest is Dr. F. Hoffmann's biography of Ferdinand F. Meyer as a New York chemist, *Pharm. Rundschau*, 1894, xii., 125, and of more general interest, Professor Schaer's history of Mayer's alkaloid reagent, *Pharm. Rundschau*, xii., 142).

This iodine solution was tried briefly by Schweissinger in 1885 (*Arch. Pharm.*, 1885, 611), and at length by Kippenberger in 1895 (K. Kippenberger, 1895; *Ztschr. Anal. Chem.*, xxxiv., 317; xxxv., 407, 422), but both seem to have obtained the lower periodides, at least in part, in their methods of estimation. The last-named author proceeded upon a volumetric deduction of a general formation of tri-iodides, and sought to so vary the conditions as to support the factor of a tri-iodide. In 1896, Gomberg (*Journ. Amer. Chem. Soc.*, xviii., 331), along with his production of caffeine perhalides above referred to, established the volumetric estimation of caffeine in acidulated solutions as a pentaiodide, and this was used, with a method of extraction from Kola, throughout the work of Mr. Knox and one of us (Knox and Prescott, *Proc. Am. Pharm. Assoc.*, xliv., 128; xlv., 131; *Journ. Amer. Chem. Soc.*, xix., 63; xx., 34) upon the caffeine compound of kola with complete satisfaction.

The Higher Periodides in respect to Constancy of Composition.

The number of the periodides of pyridine is representative of the fact that most of the alkaloids of pyridine-derived constitution will form each more than one periodide, according to conditions. We find it is more expedient to secure the exclusive formation of the higher periodide, by needful conditions, than that of any other periodide obtainable. The higher periodides are not surpassed in completeness of precipitation, and they are sufficiently stable. At least this is true of those alkaloids included in this report. In future reports we desire to be able to give analyses of all the readily obtained periodides of each of the alkaloids reported upon in this article.

If we add the iodopotassium iodide solution to the solution of an alkaloidal salt, keeping from the beginning to the end the alkaloid in excess, it is generally the lowest periodide (in most cases a tri-iodide) that is formed, but if the order be reversed and the alkaloidal solutions added to the iodopotassium iodide solution, keeping all the time a large excess of iodine, it is generally the highest periodide that is formed. We have found this rule to hold good with atropine, strychnine, brucine, aconitine, and several other alkaloids. It was mainly the lower periodides of alkaloids that were made and described by Jörgensen; they are generally very stable, and can be easily obtained in crystalline form by crystallisation from some suitable solvent. As to the higher periodides, some of them are stable enough to be re-crystallisable; many others are easily decomposed in solution into free iodine and lower periodides. Atropine enneaiodide belongs to the first class; strychnine heptaiodide and brucine heptaiodide belong to the second.

Following the above-mentioned rule, we have succeeded in obtaining an enneaiodide of atropine, $C_{17}H_{23}NO_3HI\,I_8$; a heptaiodide of strychnine, $C_{21}H_{22}N_2O_2HI.I_6$; a heptaiodide of brucine, $C_{23}H_{26}N_2O_4HI.I_6$, and, as it is probable, a tri-iodide and a heptaiodide of aconitine. The tetraiodide of morphine, obtained by Jörgensen is the only periodide of morphine that we have been able to make by precipitation.

* Prescott, the Periodides, *Journ. Am. Chem. Soc.*, xvii., 775; *Pharm. Rundschau*, xiii., 233. Prescott and Trowbridge, Periodides of Pyridine, *Journ. Am. Chem. Soc.*, xvii., 859. Flinterman and Prescott, Dipyridine Methylene Dibromide, *Ibid.*, xviii., 28. Prescott, Pyridine Alkyl Iodides, *Ibid.*, xviii., 91. Trowbridge, Periodides of Pyridine, *Ibid.*, xix., 322. Trowbridge and Diehl, Halides and Perhalides of Pyridine, *Ibid.*, xix., 558.

† See paper by Gomberg read at Boston meeting of the American Chemical Society, August, 1898, and to be published in a subsequent number of the *Journ. Am. Chem. Soc.*

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These compounds are of the common order of alkaloidal hydriodide periodides. The single atom of iodine in the normal hydriodide is transposed by silver nitrate solution with precipitation, but does not respond to reducing agents. The rest of the iodine, being additive to the first atom of this element, is very easily taken up by reducing agents, such as sulphur dioxide, a thiosulphate, or powdered zinc.

Preparation of the Higher Periodides in Purity for Analysis.

The periodides, of which analysis is given in this paper, were all made according to the following method:—1 grm. of the alkaloid was dissolved in about 200 c.c. of water acidulated with sulphuric or hydrochloric acid, and the solution poured, in small quantities at a time, into 500 c.c. of water containing 1 per cent free iodine and 1½ per cent potassium iodide. After shaking until the liquid became perfectly clear, the mother-liquor was removed in filtration by means of a pump, the precipitate well washed with cold water, and dried first on porous plates and then in a vacuum over sulphuric acid. For the aconitine triiodide the order of mixing was reversed, and an excess of aconitine kept during the whole operation. After drying, the precipitate was re-crystallised from alcohol. These periodides, so prepared, were subjected to analysis by the method given under atropine below, and as stated further under the several alkaloids, and from the results of the analysis the volumetric factor of free iodine for each alkaloid was determined.

Atropine Enneaiodide and its Analysis.

The enneaiodide, obtained as above described, is a very dark brown, almost black powder, quite permanent in dry air, and has only a slight odour of iodine. It is very difficultly soluble in ether, chloroform, benzene, or carbon disulphide, but is soluble in alcohol, very freely when hot. In cold water it is insoluble; hot water decomposes it quickly; it is also decomposed by concentrated solutions of potassium iodide. At 90° C. it commences to give up iodine vapours, and at 140° C. melts to a dark liquid. To obtain it in crystalline form it is first washed with a little cold alcohol to remove traces of free iodine, and then dissolved in warm alcohol. On cooling it crystallises out in dark green prisms and leaflets, having the same properties as the non-crystallised body. In analysis we estimated the additive iodine volumetrically, and the total iodine both gravimetrically and volumetrically.

To estimate the additive iodine a small quantity of the enneaiodide is dissolved in very little alcohol, an excess of a standardised solution of sodium thiosulphate added, and the excess titrated back with a standard solution of iodine, using starch as the indicator.

For total iodine the substance is covered with an excess of powdered metallic zinc and some water, and then boiled gently for ten or fifteen minutes, taking care to prevent loss by spurting; the mixture is then thrown upon a filter, and the containing flask and the filter are thoroughly washed with hot water. The iodine in the zinc iodide thus formed can either be estimated by precipitation with silver nitrate and nitric acid, and weighing as silver iodide, or it is precipitated with an excess of a standardised solution of silver nitrate, and the excess titrated back with a standard solution of ammonium thiocyanate, using ferric nitrate as indicator.

In the following analyses the standard silver nitrate solution was made to correspond with 1 per cent of iodine, and the ammonium thiocyanate solution to correspond, c.c. per c.c., with the silver nitrate solution. The standard solution of iodine contained 1 per cent of iodine, and the sodium thiosulphate solution corresponded, c.c. per c.c., with the iodine solution.

Analysis of the Atropine Enneaiodine not Re-crystallised:—In the volumetric estimation for total iodine, 0·15225 grm. required 12·2 c.c. of the silver nitrate solution. For the iodine removed by reduction, 0·19255 grm. required 13·7 c.c. of the thiosulphate solution.

	Calculated for $C_{17}H_{23}NO_3 \cdot HI \cdot I_8$.	Found.
Iodine by reduction	70·88	71·15
Total iodine	79·74	80·13

In the gravimetric estimation from 0·218 grm. 0·3207 grm. silver iodide was obtained.

	Calculated for $C_{17}H_{23}NO_3HI \cdot I_8$.	Found.
Total iodine	97·74	79·48

Analysis of the Atropine Enneaiodide Re-crystallised from Alcohol.—The methods employed were the same as with the non-recrystallised compound, and the standard solutions of the same strength.

In the volumetric estimation of total iodine, 0·12685 grm. required 10·1 c.c. of the silver nitrate solution. For the iodine removed by reducing agents, 0·23105 grm. required 16·4 c.c. of the thiosulphate solution.

	Calculated for $C_{17}H_{23}NO_3 \cdot HI \cdot I_8$.	Found.
Total iodine	79·74	79·62
Iodine by reduction	70·88	70·98

In the gravimetric estimation of total iodine, 0·2031 grm. gave 0·30035 grm. silver iodide.

	Calculated for $C_{17}H_{23}NO_3 \cdot HI \cdot I_8$.	Found.
Total iodine	79·74	79·90

The constitution of the compound is that of atropine hydriodide octaiodide. The alkaloidal hydriodide is formed, in the (acidulated) solution, by transposition of the alkaloidal salt taken with potassium iodide. Thus:—

$$C_{17}H_{23}NO_3 \cdot HCl + KI + I_8 = C_{17}H_{23}NO_3 \cdot HI \cdot I_8 + KCl.^*$$

Therefore the ratio of the free iodine consumed, to the absolute atropine, is the ratio of I_8 to $C_{17}H_{23}NO_3$, equal to ratio 1012·24 to 288·38, or of 1 of iodine to 0·2849 of atropine.† And 1 c.c. of decinormal iodine solution consumed is equivalent to 0·0036048 grm. of the atropine. *This decinormal factor* was found to hold good under the control estimations reported further on.

(To be continued).

ON THE CAUSE OF THE RETENTION AND RELEASE OF GASES OCCLUDED BY THE OXIDES OF METALS.‡

By THEODORE WILLIAM RICHARDS.

In a recent critical discussion of Stas's work upon the atomic weight of carbon, Dr. Alexander Scott (*Journ. Chem. Soc. Trans.*, 1897, lxxi., 559), of London, had occasion to repeat some observations made at Harvard several years ago (*Proc. Amer. Acad.*, xxvi., 281; *Z. Anorg. Chem.*, i., 196). According to these observations, cupric oxide made from cupric nitrate had been found usually to contain several times its volume of occluded gases, chiefly nitrogen, and moreover it was shown that this gas resulted from the decomposition of minute traces of residual nitrate confined in the inmost recesses of the masses of oxide. Dr. Scott, however, could not find as much as one-tenth of this amount of gas in his material. Since he was unable to explain the apparent discrepancy, it is

* For experimental verification of this equation see a later paragraph in the *Journ. Am. Chem. Soc.*

† The atomic weights taken were those of L. Meyer and K. Seubert, H=1.

‡ Contributions from the Chemical Laboratory of Harvard College. From the *Proceedings of the American Academy of Arts and Sciences*, xxxiii., No. 23; also *American Chemical Journal*, November, 1898.

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one of the objects of the present paper to shed a clearer light upon the subject.

The essential point which escaped Dr. Scott's notice is this:—The temperature of ignition is the most important condition determining the amount of the occluded gases. When the temperature is very high, nearly all of the imprisoned impurity is set free. To quote Dr. Scott's words, his oxide was exposed "for varying times to a full red heat in a muffle heated with gas." It is well known that at a temperature of about 1000° cupric oxide melts, with a very considerable loss of oxygen. It is obvious, then, that temperatures in this neighbourhood are quite out of the question when the atomic weight of copper is concerned; hence, among the many experiments made by me in 1891, only three dealt with material which had been heated above 700°. The evidence of these three experiments (Nos. 59, 81, and 95) is unanimous in showing that most of the occluded impurity is set free at bright redness, and the first two of them agree quantitatively with the results of Dr. Scott.

Although it is thus evident that the English and American results are in no way inconsistent, I decided to repeat a part of the work, in order to obtain a more certain estimate of the various temperatures corresponding to the varying conditions of the cupric oxide. In my previous paper the higher degrees had been merely guessed, for they were not directly concerned in the point then under consideration.

The usual modes of determining high temperatures —the calorimeter, the air-thermometer, the bolometer, the meldometer, the platinum-iridium thermopile, &c.— are somewhat troublesome to use for a brief series of experiments of the present kind, so that it seemed best to determine the several temperatures approximately by finding for each temperature two substances, whose melting-points were respectively above and below the point in question. For instance, an intensity of heat which would melt pure argentic bromide, but not pure argentic chloride, must be between 427° and 451°, a grade of accuracy more than sufficient for the present purpose. This method of determining the temperature has the great advantage of providing an approximate self-registering thermometer, occupying very small space and needing no connection with the outside air. The usefulness of the method obviously depends upon the number of substances easily obtained in a pure state, whose melting-points are accurately known. For such knowledge of high melting-points we depend mainly upon four researches—those of Carnelley (*Journ. Chem. Soc.*, 1876 and 1878, xxix., 489; xxxiii., 273), Le Chatelier (*Bull. Soc. Chim.*, 1887, xlvii., 300), Meyer, Riddle, and Lamb (*Berichte der Deutsch. Chem. Gesell.*, 1895, xxvii., 3129), and Ramsay and Eumorfopoulos, *Phil. Mag.*, 1896 [5], xli., 360). Unfortunately the results of these four investigations do not always agree, their disagreement affording evidence of the great difficulty of measuring accurately high temperatures. At first sight the fact of the existence of such discrepancy might deter one from adopting this standard of reference, but further consideration leads to exactly the opposite conclusion. The melting-points of pure salts must be an unchangeable standard, and the uncertainty of our knowledge regarding them must be largely due to experimental difficulties in the thermometric manipulation. These difficulties, if so serious in researches where everything was favourable to accuracy, must be largely augmented in a research like the present one, in which the temperature could not be made the sole issue of the experiment. Hence the melting-point of a pure salt is the safest possible standard. The following table gives in parallel columns the salts chosen for the present scale of temperature, with the results of the four investigations, and the values of the melting-points selected as the most probable.

The most serious discrepancies are to be noticed in the cases of potassic and sodic chlorides, where the respective averages have been chosen as the most probable values.

Temperature Scale.

	Carnelley Calorimeter.	Le Chatelier Thermopile.	Meyer Air Therm.	Ramsay Meldometer.	Value Selected.
Potassic nitrate ..	339	—	—	339	339
AgI, 2AgBr, 2AgCl	383	—	—	—	383
Argentic bromide	427	—	—	426	427
Argentic chloride	451	—	—	460	451
Plumbic chloride	498	—	—	447	498
Argentic iodide ..	527	—	—	556	527
Sodic biborate ..	561	—	—	—	561
Lithic chloride ..	598	—	—	491	598
Thallous sulphate	632	—	—	—	632
Strontic nitrate..	645	—	—	570	645(?)
Potassic bromide	699	—	722	733	3720
Potassic chloride	734	740	800	762	760
Sodic chloride ..	772	775	815·4	792	790
Sodic carbonate	814	810	849	851	830
Strontic chloride	825	840	832	796	835(?)
Sodic sulphate ..	861	867	863	884	865
Baric chloride ..	860	—	921	844	920(?)
Potassic sulphate	—	1045	1078	1052	1060

These averages are almost identical with the figures obtained by Ramsay and Eumorfopoulos. On the other hand, Joly's meldometer, used by these investigators, seems to have been much less satisfactory at lower temperatures; for their melting-points of plumbic chloride and lithic chloride are widely different from Carnelley's. Repeated qualitative experiments have convinced me that plumbic chloride is less easy to melt than argentic chloride, and lithic chloride less easy to melt than argentic iodide; therefore Carnelley's calorimetric results have been adopted here as the more accurate. Strontic nitrate, and strontic and baric chloride, all begin to decompose in the air at or near their melting-points; undoubtedly this fact is responsible for the very low results obtained by Ramsay and Eumorfopoulos in these cases. Obviously such salts cannot be relied upon as trustworthy thermometers, unless one takes the precautions observed by Meyer, Riddle, and Lamb, in their work with the air thermometer. One is reminded of the interesting work of Hill upon changeable organic melting-points (H. B. Hill, *Proc. Amer. Acad.*, xxiii., 219). The other substances in the list are sufficiently stable, and are easily obtained in a pure state. In the light of Le Chatelier's complete confirmation of Carnelley's results by means of the pyrometric thermopile, it is odd that the lamented Victor Meyer accorded Carnelley so little credit as he has done.

It is needless to state that pains was taken to eliminate impurities from these substances by re-crystallisation or other suitable means, and to dry the salts thoroughly, in the work which follows. If the temperature was below 800°, the dry coarsely powdered substances were contained in small melting-tubes of the hardest Jena glass, sealed while hot at both ends, and sometimes provided with a small platinum sinker to show whether or not the salt had liquefied. If, on the other hand, the height of the temperature excluded glass, the substances were contained in small cups beaten into stout strips of platinum foil. The small amount of impurity taken from the glass tubes in which some of the substances were melted could hardly have had much effect on the melting-points until after a considerable mass of the substances had been melted; but then their mission had been fulfilled.

The table above might well be amplified to cover a wider range, as well as smaller differences of temperature, but such an amplification would constitute a research of some magnitude in itself. For present purposes the above will suffice.

Two forms of apparatus were used for determining the amount and the composition of the occluded gases. The

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first was identical in every respect with the most convenient of the three forms described in the original paper (*Proc. Amer. Acad.*, 1891, xxvi., 284). It consists of several bulbs blown in the bend of a glass tube bent at a right angle. One arm of the tube is temporarily closed by a stopcock (not shown in the cut in the original paper, although mentioned in the letterpress), and in this arm the gas, evolved in the bulbs by the solution of the cupric oxide in acid, is collected and measured over boiled water. When necessary the gas may be readily removed through the stopcock at the end of the arm; if a gas burette is attached here, of course the gas may be analysed at once without further trouble.

For most of the experiments, however, Scott's modifications of another of the original forms (*Proc. Amer. Acad.*, xxvi., 285, middle of page) was used. The mode of operating this apparatus was essentially similar to the method just described, although the bent tubes and bulbs are replaced by a small flask and funnel-tube. Scott's addition of a side tube to remove the displaced water distinctly increases the convenience and accuracy of the contrivance. For the details his paper should be consulted.

The two pieces of apparatus give identical results, which cannot be far from the truth. If at all in error the amount of gas collected must be too small rather than too large, for both oxygen and nitrogen are slightly soluble in water. This consideration was verified by fusing a specimen of oxide (another portion of which had been repeatedly analysed in the usual fashion) with carefully prepared acid potassic sulphate in a Sprengel vacuum. The amount of gas evolved by this treatment was slightly greater, but only slightly greater, than the amount obtained by the usual method, and its composition was essentially identical with that of the gas collected over boiled water. Since the question is one of relation, rather than of absolute values, the method involving the use of aqueous solutions was adopted because of its far greater ease of execution. Pains was taken to have the conditions of the solution of the oxide always as nearly as possible the same, so that the results should be strictly comparable with one another.

The first object of the present paper is to show more clearly the relation between the amount of gas retained by the oxide and the temperature used in its ignition. The material employed in these experiments was prepared by dissolving pure copper wire or electrolytic copper in pure nitric acid, and converting by heat the re-crystallised cupric nitrate into basic nitrate and finally into oxide.

(Note.—It is interesting to note that the hydrate of cupric nitrate, which crystallises from hot solutions, probably has the formula $3Cu(NO_3)_2.8H_2O$ (analogous to cadmic sulphate), not $Cu(NO_3)_2.3H_2O$ (Graham), as is usually supposed. Following are the analyses of three separate preparations, dried over moist potash (which does not dehydrate the crystals at ordinary temperatures) proving this point:—

(1) 0·1739 grm. of crystals yielded 0·0471 grm. of copper .. .. = 27·08 p.c.
(2) 0·6310 grm. of crystals yielded 0·1705 grm. of copper .. .. = 27·01 „
(3) 1·2897 grms. of crystals yielded 0·3448 grm. of copper .. .. = 26·73 „

Average = 26·94 „

Theoretical value for $Cu(NO_3)_2.3H_2O$ = 26·20 per cent of copper.
Theoretical value for $3Cu(NO_3)_2.8H_2O$ = 26·98 per cent of copper.
Theoretical value for $2Cu(NO_3)_2.5H_2O$ = 27·35 per cent of copper.

The crystals analysed in No. 3 above were large and undoubtedly contained included mother-liquor. Whether or not other hydrates exist, and what the transition temperatures may be, I did not take the trouble to discover. Much of our present data regarding water of crystallisation has been rounded off in the manner indicated above. Undoubtedly many more such irregular ratios as 3 : 8 really exist than we are prepared at present to believe).

Platinum vessels were used throughout, whenever heating was necessary, excepting that one or two of the first ignitions were conducted in a porcelain boat. Three preparations of the oxide were made; one by the rapid decomposition of the nitrate, another by more gradual application of heat, and a third by the very slow action of a temperature just barely sufficient to effect the desired change. This temperature had been previously found by a special experiment to be about 275°, if the products of the decomposition remain in contact with the cupric oxide. The first of these preparations was the most coherent, and was capable of retaining the most gas; the second was less coherent and retained less gas; and the last was the most powdery, and retained even less gas. Thus it is manifest that the physical condition of the solid is a factor in the question.

These specimens of the oxide of copper were subsequently ignited at varying temperatures for varying lengths of time in two different forms of furnace. For the first series a large tube or small muffle of Berlin porcelain

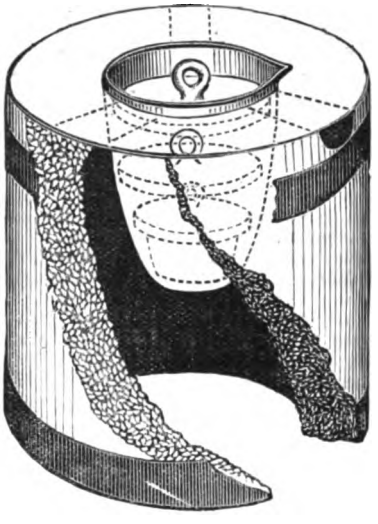

Fig. 1.

capable of being heated to 1200° or more in a Fletcher furnace was used; but since it was found difficult to maintain the tube at a constant temperature throughout, this arrangement was later abandoned. All the subsequent ignitions were performed in a double crucible arranged in the manner shown in the diagram, the low platinum crucible or capsule used to contain the cupric oxide being protected from radiation and convection by a number of superimposed crucible lids. The outer glazed porcelain crucible and the layers of asbestos board covering the draught holes united in excluding the products of combustion of the illuminating gas from the contents of the inner capsule. By means of this furnace, fed with a constant gas supply burning from a fourfold Bunsen burner, a surprisingly constant and uniform temperature may be maintained for an indefinite length of time.

(To be continued).

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NOTICES OF BOOKS.

A Text-book of Physiologcal Chemistry. By Olof Hammersten. Authorised Translation from the Author's Enlarged and Revised Third German Edition, by John A. Mandel. Second Edition. New York: John Wiley and Sons. London: Chapman and Hall, Lim. 1898. Pp. x.-705. 8vo. Plate.

The author of this treatise, who is Professor of Medical and Physiological Chemistry in the University of Upsala, first published his "Lärobok i fysiologisk kemi och fysiologisk kemisk analys" in 1883. It did not at first attract the attention of students outside of Scandinavia; but after the publication of a second edition, in 1889, it was translated into several languages; a German version appeared in 1891, a Russian in 1892, an Italian in 1893, and the first English version—translated from the German by Professor Mandel—in the same year. The present volume is a translation of the third German edition, no changes or additions having been made except to incorporate Hammersten's Addenda in the text.

The volume of seven hundred large pages is divided into the following chapters:—

I. Introduction. II. Protein substances. III. Carbohydrates. IV. Animal Fats. V. The Animal Cell. VI. The Blood. VII. Chyle, Lymph, Transudations and Exudations. VIII. The Liver. IX. Digestion. X. Tissues of the Connective Substance. XI. Muscle. XII. Brain and Nerves. XIII. Organs of Generation. XIV. Milk. XV. The Urine. XVI. The Skin and its Secretions. XVII. Chemistry of Respiration. XVIII. Metabolism.

The arrangement of the subject-matter was based upon the manner in which physiological chemistry is studied in Sweden, where physiologico- and pathologico-chemical laboratory practice is obligatory on all students of medicine. The analytico-chemical part is distinguished by setting the type without leads, thus making it a handbook for the laboratory.

This volume gives students a most comprehensive survey of the present status of physiological chemistry, and will be found indispensable in the library of every physician who wishes to keep abreast of the times.

Complaint is often made that medical men are not scientific; the researches chronicled in Hammersten's valuable treatise, properly digested, will go far to remove this reproach.

Numerous references to literature and an Index are good features of this admirable work. H. C. B.

A Dictionary of Perfumes used in Soap-making. By A. M. Garance. London: Maclaren and Sons, 37 and 38, Shoe Lane, E.C. Glasgow: 128, Renfield Street.

Soap-makers and perfumers generally will find this book of great use. It being a first attempt at arranging these receipts in dictionary form, the author does not claim completeness, but asks the collaboration of his readers to make it so. We find from this book that a great many perfumes are not even remotely connected with the flower from which they take their names: thus we learn that, although the lily yields a delicate perfume, "in toilet soaps the odour is always imitated"; narcissus, "the odour is imitated by the following mixture," &c.; verbena gives a very fine perfume, "hardly ever used by the perfumer, but a most successful imitation," &c. We are glad to see that English lavender is superior to any other: this is remarkably illustrated by the list of prices of oils of lavender, ranging from one shilling and threepence per pound to six and threepence for that from French picked flowers, while that from Mitcham lavender commands no less than four guineas

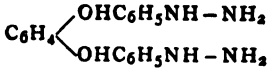
There is a Botanical Appendix at the end, and also a good Index, which add much to the value of the work.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

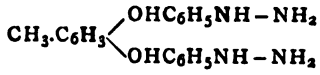
Note.—All degrees of temperature are Centigrade unless otherwise expressed.

Comptes Rendus Hebdomadaires des Séances, de l'Académie des Sciences. Vol. cxxvii., No. 18, October 31, 1898.

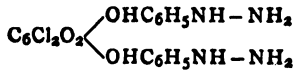
Action of Phenylhydrazin on Chloranilic Acid.—A. Descomps.—By the reaction of phenylhydrazin on phloroglucin in alcoholic solution Baeyer and Kochendörfer obtained a body corresponding to the formula $C_6H_3(OH)_3(C_6H_5NH-NH_2)_3$. On the other hand, Seyewitz obtained compounds analogous to hydroquinone and orcine, represented respectively by the formulæ—



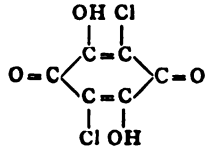
and—



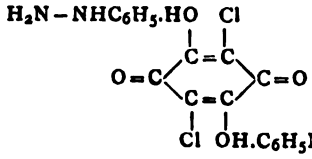
The action of phenylhydrazin on chloranilic acid gave a crystalline body analogous to the above. It has the formula—



The formula ascribed by Kehrmann, Hantsch, and Schniter to chloranilic acid is—



Hence the body obtained by reacting with phenylhydrazin will be represented by—



No. 19, November 7, 1898.

Preparation of Lithium Ammonium, Calcium Ammonium, and the Amides of Lithium and Calcium.—Henri Moissan.—Potassium, sodium, lithium, and calcium combine with ammonia gas, and the ammonium compounds formed decompose at ordinary pressure at the temperature +70° for lithium, +20° for calcium, −2° for potassium, and −20° sodium. Lithium and calcium ammonium take fire in contact with air at ordinary temperatures, and correspond to the formulæ $NH_3.Li$ and $(NH_3)_4Ca$. These two compounds do not dissociate at ordinary pressure and temperature in an atmosphere of ammonia gas. They are stable compounds, which lend themselves to addition and substitution reactions more easily than the ammonium alkalis.

Preliminary Notice of the Presence of Free Hydrogen in Atmospheric Air.—Armand Gautier.—The author has conducted a long series of researches on specimens of air taken from high mountain regions and over the sea. He finds that free hydrogen is present in the proportion of about 1·5 volumes to 10,000 volumes of air. The proportion of hydrogen is considerably greater in the specimens of pure air than in specimens taken from the

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neighbourhood of towns, whilst the proportion of combustible carbon compounds is correspondingly less.

Properties of Triethyl Boric Ether.—H. Moissan.—Boron is said to be a trivalent element, capable, like carbon, of combining with itself, and by condensation, a partial dehydration of its fundamental hydrate, $B(OH)_3$, forming new hydrates to an indefinite extent; *e.g.*—

$$\begin{array}{lll} B(OH)_3, & B_2H_4O_5, & B_3H_5O_7 \ldots. \\ BO_2H, & B_2H_2O_4, & B_3H_3O_6 \ldots. \\ & B_2O_3, & B_3HO_5 \ldots. \end{array}$$

Hence, theoretically, the number of corresponding ethers is also unlimited. But, in fact, only two classes of boric ethers are known, viz., the tri-alcoholic, BO_3R_3, and the mono-alcoholic, BO_2R (discovered by Ebelmen in 1846, and investigated by Schiff in 1867). The former are liquid bodies, capable of distillation, and of definite composition; the latter have yielded no consistent results on analysis, and are incapable of distillation and crystallisation. To complete the study of the tri-alcoholic borates, the author of this paper has chosen the case of the triethyl borate, $BO_3(C_2H_5)_3$. It was prepared according to Schiff's method, by the direct action of B_2O_3 on absolute alcohol at 120° (under a pressure of about 2 atmospheres). $B_2O_3+3C_2H_5OH=BO_3(C_2H_5)_3+BO_3H_3$, triethyl borate, is a mobile, colourless liquid, of density 0·887 at 0°, boiling at 119·5°, and a non-conductor of electricity; it is immediately saponified by water, and of all the anhydrous reagents with which it was treated, chlorine, alkaline ethylates, and alkalis, alone gave definite results. Chlorine replaced the hydrogen of ethyl borate, giving at the end of the reaction a gelatinous mass. The increase of weight indicated the entrance of five chlorine atoms into 1 molecule of $BO_3(C_2H_5)_3$. On treating with potash an oil was obtained which partially decomposed on distillation, and possesses the formula $C_4H_7Cl_3O$, or—

$$\begin{matrix} CHCl_2.CHCl \\ C_2H_5 \end{matrix}\!\!>\!O.$$

On treating triethylborate with sodium alcoholate, dissolved in absolute alcohol, a white crystalline powder was finally obtained, possessing the formula—

$$BO_3(C_2H_5)_3+C_2H_5ONa.$$

This compound is easily decomposed by water, but can be heated to 200° without decomposition; it demonstrates the pentavalence of boron.

Combinations of Phenylhydrazin with the Halogen Salts of the Alkaline-earth Metals.—J. Moitessier.—With anhydrous calcium chloride, dissolved in alcohol, phenylhydrazin yields the stable compound—

$$CaCl_2.2(C_6H_5NH{\cdot}NH_2),$$

crystallising on cooling. Anhydrous strontium chloride reacts similarly, but the combination is easily decomposed by the ordinary solvents. Phenylhydrazin calcium bromide, $CaBr_2.4(C_6H_5NH{\cdot}NH_2)3H_2O$, was obtained by adding the theoretical quantity of phenylhydrazin to calcium bromide dissolved in water, and evaporating the solution. Crystals are obtained, soluble in alcohol, and decomposed by boiling benzene. Anhydrous strontium bromide also combines with phenylhydrazin, 1 molecule of the former to 2 molecules of the latter. A hydrated combination can also be obtained. The iodide, $SrI_2.4(C_6H_5NH{-}NH_2)$, is similarly prepared, and consists of deliquescent prismatic crystals. Phenylhydrazin does not combine with the fluorides of the alkaline earths, but such combinations are possible with certain fluorides of the magnesium group, notably zinc fluoride. It also combines with cuprous salts, with lithium bromide, and with oxalates and benzoates of the magnesium group.

Estimation of Gelatin in Gums and Food Substances.—A. Trillat.—It is known that formaldehyd, when heated with albumenoid substances, renders the latter insoluble, and this property may be utilised for detecting and estimating the gelatin fraudulently added to gums and food substances. A description of the process is given as applied to the case of gum arabic. It is easily possible, by means of this process, to distinguish artificial jellies from gelatin and natural vegetable jellies.

No. 20, November 14, 1898.

The Preparation of Crystalline Tungsten by Electrolysis.—A. Hallopeau.—The author obtains crystalline tungsten by electrolysing paratungstate of lithium. He uses platinum electrodes, and passes a current for three hours. At the end of that time the resulting mass is repeated, treated with boiling water, then with strong hydrochloric acid, and lastly with a boiling lithia solution. At the end of these washings there remains a crystalline substance consisting of tungsten mixed with a certain quantity of platinum from the electrodes. The tungsten is found in opaque crystals, usually in the form of needles. The composition of these crystals is proved by analysis.

Volumetric Estimation of Boric Acid.—M. Copaux.—The author refers to a former paper in which is given the preparation of certain boric compounds. The present paper treats of the mode of analysis of the same compounds. It is found that though the volumetric estimation of free boric acid titrated with an alkali is an impracticable method, yet the acid can be estimated volumetrically as follows:—The weighed material dissolved in a small volume of water, coloured yellow by two drops of helianthine, then saturated with sulphuric or hydrochloric acid till the solution is red. The boric acid is now displaced by a strong acid, and if a known volume of glycerin is added the solution can be titrated against soda solution, phenolphthalein being used as an indicator.

New Halogen Derivatives of Guaiacol and Veratrol.—H. Cousin.—The author discusses the preparation and properties of the following new bodies:—Trichlor-guaiacol, trichlor-veratrol, dibrom-guaiacol, tetrabrom-guaiacol, and tribrom-veratrol.

A New Sugar accompanying Sorbite.—Camille Vincent and J. Meunier.—Examination of the mother-liquors from the preparation of sorbite from certain fruits, led the authors to the discovery of a homologous body capable, like sorbite, of combining with benzaldehyd. This new alcohol is octatomic, having crystalline derivatives, itself, however, only having been obtained as a syrup. The sorbite solution is concentrated, to effect deposition of the crystals of sorbite, the non-crystallisable mother-liquor treated with the sorbose bacterium for conversion of any remaining sorbite, and, finally, the unchanged liquid treated with benzaldehyd in presence of sulphuric acid, and thus the new alcohol isolated as an acetal. The latter crystallises from chloroform, therein differing from the acetal of sorbite, which is not crystalline. Analysis gives it the formula of the dibenzoic acetal of an alcohol, $C_8H_{18}O_8$.

Derivatives of Natural Methyl-heptenone.—Georges Leser.—Not suitable for abstraction.

Volumetric Estimation of Ethyl-aldehyd.—X. Rocques.—The author makes an addition to his recent paper on the estimation of ethyl-aldehyd by means of acid sulphites, to the effect that temperature exercises a considerable influence on the reaction. At a temperature of from 25° to 30° the reaction is complete in less than twenty-four hours, whilst at 15° it is not complete after a lapse of forty-eight hours.

Method of Formation of Indigo in the Industrial Processes of Extraction. Diastasic Functions of the Indigofera.—L. Bréandat.—For investigation of the ferment by means of which indigo is obtained from the glucoside indican contained in the Indigofera and other plants, the author took the case of *Isatis alpina*. The results of treating the leaves of this plant in various ways pointed to the following conclusions:—(1) The micro-organisms play no conspicuous part in the fermentation.

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(2) This plant contains a hydrating and oxidising diastase, the former converting the indican into indigo-white and indiglucine, the latter oxidising the indigo-white to indigo-blue. (3) All plants capable of yielding indigo contain these two diastases.

Journal de Pharmacie et de Chimie, vol. viii., No. 3.

The Enamel of Cooking Utensils.—L. Barthe.—In a recent case of poisoning, by which one person lost his life and several others were made very ill, the poison was said to be traced to an enamelled iron saucepan of the familiar kind, white inside and deep blue outside. Some French enamels have been found to contain as much as 52·51 per cent of oxide of lead and 3·74 per cent of arsenic acid. The enamelled utensil in question, however, did not contain either of these, but did contain large proportions of silica, tin, and aluminium, small quantities of zinc, lime, and potash, and traces of iron and cobalt; the author is therefore of the opinion that in this case the enamel was not to blame.

Estimation of Boric Acid.—M. Vadam. —Already inserted.

No. 4.

The Action of Soluble Ferments on the Pectic Products of Gentian Root.—E. Bourquelot and H. H. Hérissey.—The authors have already shown that there is a certain analogy between the hydration by warm water of the principle of gentian which furnishes pectine, and that of starch. They have also shown that the pectine of this plant, submitted to the hydrolysing action of dilute warm sulphuric acid, gives a reducing sugar—arabinose. They now describe experiments to determine whether there are not existing soluble ferments capable of acting on pectose or pectine, and they find that *Aspergillus niger* has a hydrating action on pectose: this action is confirmed by several experiments in the case of pectine; all the experiments with *Aspergillus* and with saliva gave negative results.

MISCELLANEOUS.

Illustrated Catalogue of Scientific Apparatus, issued by Messrs. W. and J. George, Lim.—We have received a complete Illustrated Catalogue of Scientific Apparatus from Messrs. W. and J. George, Limited, who have taken over the business formerly carried on by F. E. Becker and Co., of Hatton Wall, E.C. It includes many new and recently devised pieces of apparatus which will be welcome to chemists. The illustrations are particularly good and numerous. Among the novelties are a series of torsion balances, ranging from a chemical balance to turn with a hundredth of a grain, to druggists' scales with a load capacity of twenty pounds. This form of balance has been very little used in England, and is likely to prove of value, especially where it is exposed to rough usage. Lovibond's tintometer, with its many adaptations; a complete series of hot-air engines and turbines, from 1-60th of a horse-power and upwards, with a great many pieces of apparatus for rocking, shaking, stirring, &c.; Röntgen's apparatus and Wimshurst machines. Crookes's tubes, and apparatus for illustrating Tesla's, Hertz's, and Marconi's experiments, are also described. The section devoted to bacteriological apparatus is complete, and contains some of the latest additions. With the chemical apparatus are included many new items; among others we note the long-wished-for steel tube cork-borer. A special point is made of an efficient chemical balance with agate knife edges and bearings sensitive to 1 m.grm., at a price which places it within the reach of any student. Chemists and physicists generally will be grateful to Messrs. George and Co. for having placed in their hands such a complete list of apparatus.

MEETINGS FOR THE WEEK.

Monday, 16th.—Society of Arts, 8 (Cantor Lectures). "Bacterial Purification of Sewage," by Dr. Samuel Rideal.

Tuesday, 17th.—Royal Institution, 3. "The Morphology of the Mollusca," by Prof. E. Ray Lankester, M.A., LL.D.

Wednesday, 18th.—Society of Arts, 8. "Canals and Inland Navigation in the United Kingdom," by L. F. Vernon-Harcourt, M.A.

—— Institution of Mining and Metallurgy, 8. "The Tin Mines of Bolivia," communicated by W. McDermott. "On Minerals found in the Silver Lodes of Tatasi, and Portugalete, Bolivia," by Malcolm Roberts. "The Deep Leads of Victoria," by E. Lidgey. "Notes on Blue Asbestos," by H. F. Olds. "Notes on Dry Crushing on the Witwatersrand," by Franklin White.

Thursday, 19th.—Chemical, 8. "Researches on Moorland Waters—I. Acidity," by W. Ackroyd. "α-Ketotetrahydronaphthalene," by Dr. S. Kipping, F.R.S., and Alfred Hill. "A New Method for Preparing *as.*-Dimethyl- and Trimethyl-succinic Acids," by W. A. Bone. "Reduction of Optically Active Mono- and Di-alkyloxysuccinic Acids from Malic and Tartaric Acids," by T. Purdie, F.R.S., and W. Pitheathly, B.Sc. "Action of Ammonia on Ethereal Salts of Organic Bases," by S. Ruhemann, M.A., Ph.D. "Esterification Constants of Substituted Acetic Acids," by J. J. Sudborough, Ph.D., and L. L. Lloyd. "Di-ortho-substituted Benzoic Acids—Part IV., Formation of Salts from Di-ortho-substituted Benzoic Acids and different Organic Bases," by L. L. Lloyd and J. J. Sudborough, Ph.D. "The Thermal Effects of Dilution," by J. H. Pollok. "The Changes of Volume due to Dilution of Aqueous Solutions," by F. B. H. Wade, B. A.

—— Royal Institution, 3. "Tibet and the Tibetans," by A. Henry Savage Landor.

—— Society of Arts, 4.30. "Railways in Burma and their Proposed Extension across Yunnan," by J. Nisbet. (This Meeting will be held at the Imperial Institute).

Friday, 20th.—Royal Institution, 9. "Liquid Hydrogen," by Prof. Dewar, M.A., LL.D., F.R.S.

Saturday, 21st.—Royal Institution, 3. "Liszt" (with Musical Illustrations), by Sir Alexander C. Mackenzie, Mus. Doc.

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THE CHEMICAL NEWS.

Vol. LXXIX., No. 2043.

THE ESTIMATION OF MANGANESE BY MEANS OF POTASSIUM PERMANGANATE.

By F. W. DAW, Assoc. R.C.S., F.I.C., F.C.S.

The permanganate method of estimating manganese, although a rapid and simple method, is very generally ignored, and in some cases is held in bad repute. The cause for this perhaps is to be found in the fact that under certain conditions inconsistent results can be easily obtained. The sources of error when working on ferro and spiegel are chiefly due to three causes: firstly, non-elimination of the organic matter present; secondly, reckless addition of ZnO in large excess and in hot solutions; and thirdly, standardising the permanganate with iron instead of manganese.

To eliminate these errors I have adopted the following method, which I find gives very concordant results:—0·5 grm. of ferro or spiegel is weighed out and introduced into a wide-mouth 16 oz. Phillips beaker, and in the case of ferro 0·4 grm. of pure iron wire is added, to render the precipitation by oxide of zinc easier. The ferro or spiegel is dissolved in 30 c.c. HCl, and the iron oxidised with a few c.c. HNO_3, 15 c.c. of 50 per cent H_2SO_4 is then added, and the whole evaporated on the hot plate till fumes of H_2SO_4 are copiously evolved. When cool, water is added, the sulphates dissolved, and the solution washed out into a 1000 c.c. conical flask. Cold water is added to make up to about 500 c.c., the acid partially neutralised with Na_2CO_3, and oxide of zinc gradually added till the iron is all precipipitated, but a large excess of zinc is to be avoided. The solution containing the precipitate is without filtering brought to a boil, and standard permanganate run in till within a few c.c. of the expected amount; the flask is well shaken, and the permanganate run in, a few drops at a time, till a pink colour appears above the precipitate. This is easily observed by holding the flask on one side, covering the mouth of flask with a cloth, and waiting a few seconds till precipitate is partially settled, when a pink colour is easily seen near the neck.

The standard permanganate solution is made up by dissolving 10 grms. $K_2Mn_2O_8$ to a litre of water, and standardising it by means of ferro-manganese of known composition.

If iron is used to standardise the solution, a figure is obtained which gives low results when working on manganese. Brearley (Chem. News, lxxv., p. 15) considers this due to a small amount of carbon in the iron wire used, but the same result is found if pure ferrous ammonium sulphate is used containing no carbon.

The estimation of the manganese in the standard ferro I make by weighing as Mn_3O_4 after precipitation by bromine and ammonia. This is a method which has received a large amount of adverse criticism, but which gives very good results if worked properly. The precipitate after drying is ignited (the paper being burnt first) in a platinum crucible over the full blast of the blowpipe for three or four minutes. The precipitate after weighing is freed from silica, oxides of iron, copper, nickel, &c., by dissolving in HCl, diluting, adding ammonium acetate, passing H_2S, and filtering; this is ignited, weighed, and subtracted from the total precipitate.

The volumetric method described by Brearley (Chem. News, lxxv., p. 15) gives very fair results, but is, I think, needlessly complicated. The separation of iron and manganese by a minimum amount of sodium acetate, described there, gives a very perfect separation, not a trace being found on testing the acetate precipitate.

THE ANALYSIS OF MANTLES FOR INCANDESCENT GAS BURNERS.

By E. HINTZ.

The commercial incandescent mantles of to-day are composed almost entirely of oxide of thorium, ThO_2, to which has been added a small quantity of oxide of cerium, CeO_2, varying from 0·5 to 2·0 per cent. With the exception of a small quantity of lime they only contain traces of impurities, such as nitrate of thorium, and oxides of zirconium, neodymium, lanthanum, and yttrium. The estimation of all these bodies is an extremely delicate operation. To satisfy himself that these impurities have no appreciable influence on the luminous power of the mantle, and therefore that not much notice need be taken of these impurities in the analysis of incandescent bodies, the author has undertaken a series of photometric measurements, from which he has been able to establish the following conclusions:—

1. The oxides of zirconium, lanthanum, and yttrium up to 1 per cent do not increase the illuminating power of mantles composed of pure oxide of thorium. Oxide of neodymium increases it to a slight extent. With a consumption of 111 litres of gas per hour, the addition of 1 per cent of this oxide increases the illuminating power by 13 Hefner candles.

2. The admixture of 1 per cent of oxide of neodymium, lanthanum, or yttrium, and the addition of 0·2 to 1·0 per cent of oxide of zirconium, have no influence on the illuminating power of mantles made from thorium. The influence of 2·0 per cent of oxide of zirconium is doubtful.

3. The admixture of 1 per cent of the oxides of zirconium, neodymium, lanthanum, or yttrium has no influence on the emissive power of thorium-cerium mantles containing 0·5 per cent of lime. The lime contained in the mantles doubtless comes from the ash of the tissue used in their manufacture. It is this substance which increases the fragility of the mantles, and it should always be eliminated as far as possible.

In collaboration with H. Weber, the author has examined Knorre's method for the estimation of cerium; it is well known that this method consists in acidulating the solution of the cerous salt by sulphuric acid, and transforming it into ceric salt by boiling in presence of persulphate of ammonium. The yellow ceric compound is reduced by dilute peroxide of hydrogen to the state of a colourless cerous salt, and the excess of peroxide of hydrogen is titrated by means of permanganate. Ten atoms Fe=2 molecules $KMnO_4$=5 molecules H_2O_2=10 molecules CeO_2; consequently 56 parts Fe = 140 parts Ce = 172 parts CeO_2. To oxidise 0·2 to 0·3 grm. of cerium it suffices to use 3 grms. of persulphate of ammonium. This method applied to the analysis of thorium-cerium mantles gives good results when carried out *exactly* in the following manner.

The solution (see further on) containing about 1 grm. of ThO_2 and 0·01 grm. of CeO_2 is acidulated with 5 to 7·5 c.c. of dilute sulphuric acid (1 vol. H_2SO_4+6 vols. H_2O); it is diluted up to 200 c.c., and a part only of the persulphate of ammonium added. It is then heated to boiling for two minutes, cooled to 40—60° C., and a second portion of the persulphate of ammonium added. After a second boiling, followed by a second cooling, the remainder of the persulphate is added, and the whole boiled for ten or fifteen minutes.

Towards the end of the ebullition we add a further 2 c.c. of dilute sulphuric acid, and then cool completely, after which, by means of a burette, dilute peroxide of

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hydrogen is added drop by drop, until the yellow coloura-tion disappears; we then immediately titrate the excess of peroxide of hydrogen by means of a solution of per-manganate.

The presence of nitrates in small quantities does not interfere with the results; but acidification by nitric acid instead of sulphuric acid would lead to too low results.

The simplified method for the analysis of incandescent mantles, proposed by the author, is as follows:—

Take at least twelve mantles *before incineration*, cut off the upper and lower extremities, keeping only the middle portions, for the upper parts are frequently impregnated with hardening substance, and the lower parts are likely to contain an excessive proportion of nitrate of cerium. Weigh the middle parts, and thoroughly exhaust them with water to which a few drops of nitric acid have been added. Burn the tissue, melt the residue with bisulphate of potassium, take up with dilute hydrochloric acid, pre-cipitate with ammonia, dissolve the precipitate in nitric acid, add the solution thus obtained to the principal solu-tion, and dilute to a convenient bulk.

1st. We can detect the presence of 1 part of oxide of neodymium Nd_2O_3 in 100 parts of oxide of thorium in a portion of the liquid by its characteristic colour, and by the absorption bands observed in the spectroscope.

2nd. Precipitate part of the solution with oxalic acid, after having eliminated the excess of mineral acid by evaporation. Collect the precipitate (*a*) on a filter of hard paper, transfer this precipitate to a beaker, heat with a concentrated solution of oxalate of ammonia, dilute with water, allow to cool, filter again after the solution has been standing for a considerable time, calcine and weigh.

The precipitate may contain a small quantity of thorium, so that even in the absence of neodymium, lanthanum, and yttrium the result in oxide of cerium will be a little too high. At the same time the presence of lime affects the accuracy of the results in the same manner. In any case if the weight of the precipitate does not exceed the actual weight of the oxide of cerium by more than 1 per cent, we may safely assume that the mantles do not contain either lanthanum, neodymium, or yttrium in appreciable quantities. If the divergence is greater than 1 per cent the precipitate should be re-dissolved in sulphuric acid, and submitted to complete analysis for the detection and estimation of the earths.

To test the filtered liquid from (*a*) for oxide of zircon-ium we evaporate to dryness, calcine gently, re-dissolve in hydrochloric acid, evaporate off the excess of acid, and run the residue on to a glass plate by means of a few drops of water. Drive off this water by evaporation, then add a drop of water and a drop of binoxalate of potassium, evaporate to dryness again, and search under the micro-scope for the characteristic crystals of the double oxalate of potash and zirconium. The presence of 0·1 per cent of oxide of zirconium can be recognised by the method we have just described, even when working on only one mantle.

3rd. Evaporate off the excess of acid in a part of the solution, and precipitate with oxalic acid; calcine and weigh the precipitate which contains all the rare earths, with the exception of oxide of zirconium. The results are influenced by lime. But with mantles formed of 1·2 per cent CeO_2, 98·4 per cent ThO_2, and 0·4 per cent CaO, there is no particular disadvantage in considering lime as oxide of thorium.

4th. Titrate the cerium in a known volume of the solu-tion by Knorre's method, remembering that the presence of a small quantity of organic matter, resulting from the exhaustion by nitric acid, will necessitate the use of a slightly larger quantity of persulphate of ammonia to that indicated above. In the absence of neodymium, lantha-num, and yttrium, or in the presence of only small quantities of these bodies, the difference between the re-sults of (4) and (3) will give the oxide of thorium.—*Zeit. Anal. Chem.*, xxxvii. [2], p. 94.

ON THE USE OF OXALATE OF SODA IN VOLUMETRIC ESTIMATIONS.

By P. L. SÖRENSEN.

The author recommends the use of normal oxalate of soda to form carbonate of soda, for determining the titra-tion value of the normal acids used in volumetric estima-tions.

The pure product can be prepared in the following manner:—

One part of commercial oxalate of soda is dissolved in 32 parts of water: this makes a saturated solution at 15° C. The solution is made slightly alkaline by means of caustic soda; it is then left in a large beaker until it becomes perfectly limpid. It is then filtered to separate any impurities which may not have dissolved, notably oxalate of lime. The clear solution is evaporated to one-tenth of its original volume on a water-bath. The oxalate of soda crystallises, and the mother-liquor con-tains the greater part of the most soluble impurities, such as oxalate of potash, caustic soda, the alkaline chlorides and sulphates, &c. The crystals of oxalate of soda are filtered off, crushed, and washed several times with cold water. A second crystallisation enables us to obtain the salt in an altogether pure state.

Oxalate of soda does not contain any water of crystal-lisation; it can be heated to 125—150° without under-going decomposition. It is not hygroscopic, and can be weighed with great accuracy. A given weight of oxalate of soda can be transformed into carbonate for the pur-poses of analysis by simple calcination in a platinum crucible furnished with a tightly-fitting cover to prevent losses by projection. If a little carbon is formed it can be burnt away by partially uncovering the crucible to-wards the end of the operation.—*Zeitschr. Anal. Chem.*, xxxvi., p. 639.

A VOLUMETRIC METHOD FOR THE ESTIMATION OF GRAPE SUGAR, MILK SUGAR, AND OTHER BODIES CAPABLE OF REDUCING FEHLING'S SOLUTION.

By E. REIGLER.

This method is based on the estimation of the copper in a known volume of Fehling's solution, before and after reduction. The determination is carried out by means of Haen's iodometric method.

The cupric solution is prepared by dissolving 34·64 grms. of crystallised sulphate of copper in 500 c.c. of water. The solution of Seignette salt is prepared by dissolving 175 grms. of this salt and 50 grms. of sodic hydrate in 500 c.c. of water.

To titrate the cupric solution (once for all) we pour 10 c.c. of each of the above-mentioned solutions into a flask of 200 c.c. capacity, add 100 c.c. of water, 2 c.c. of pure concentrated sulphuric acid, and stir the whole care-fully. We then add 1 grm. of iodide of potassium dis-solved in 10 c.c. of water, shake, and allow to stand for ten minutes. We finally add 3 c.c. of starch solution, and titrate the iodine set free by means of decinormal hyposulphite, until the blue colour disappears and does not reappear until after the lapse of five minutes. If the colour comes back after this interval, no notice need be taken of it.

From the equation $2CuSO_4+4KI=2K_2SO_4+Cu_2I_2+I_2$, it follows that each c.c. of the hyposulphite solution represents 0·00635 grm. of copper. If the solutions are properly prepared 10 c.c. of the cupric solution will require 27·8 c.c. of the hyposulphite solution, corresponding to 0·1765 grm. of copper.

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For the estimation of grape sugar we add together 10 c.c. of the cupric solution, 10 c.c. of the Seignette solution, and 30 c.c. of water, in a flask of about 200 c.c. capacity. The whole is heated to boiling, and then, by means of a pipette, exactly 10 c.c. of the solution of sugar is added; this solution should not contain more than 1 per cent. The boiling is kept up for a few seconds. The precipitate is allowed to settle, which does not take long; then filter and wash with 80 c.c. of water. The filtrate is received in a 200 c.c. flask, and titrated as described above. If v be the number of c.c. of hyposulphite used, the quantity of copper reduced by the sugar will be $(27{\cdot}8-v)$ 0·00635.

The corresponding amount of sugar can then be calculated by means of Allen's tables.

Before estimating the milk sugar in milk it is necessary to remove the albumenoid matter; this is easily and completely done by means of asaprol. To 500 c.c. of water we add 15 grms. of asaprol and 15 grms. of crystallised citric acid, and filter the solution. Of this solution, which will keep indefinitely, we take 15 c.c. and add them to 10 c.c. of milk in a flask of 100 c.c. capacity, and make the volume up to the mark on the flask with distilled water. The mixture should be vigorously shaken, heated to 60°, and filtered: 20 c.c. of the clear liquid are boiled for six minutes with 10 c.c. of the cupric solution, 10 c.c. of the Seignette solution, and about 30 c.c. of water, in a flask of 200 c.c. capacity. After filtering and titrating, the formula $(27{\cdot}8-v)$ 0·00635 will give the quantity of copper reduced, and Soxhlet's table will give the corresponding amount of milk sugar present. In actual work the quantity found is expressed for 2 c.c. of milk. If the quantity of copper reduced is less than 100 m.grms., we can, without appreciable error, consider that each m.grm. of copper corresponds with 0·725 m·grm. of milk sugar.

The precipitate collected on the filter may be used for estimating the fat and the total nitrogen.—*Zeit. Anal. Chem.*, 1892, xxxvii. [1], p. 22.

ON THE CAUSE OF THE RETENTION AND RELEASE OF GASES OCCLUDED BY THE OXIDES OF METALS.*

By THEODORE WILLIAM RICHARDS.

(Continued from p. 21).

In the following table are given the new series of results showing the relation of the total volume of gas retained to the temperature used in the ignition of the cupric oxide. The gas volumes are reduced to 0° and 760 m.m. pressure, the reduction having been made by means of a Winkler-Lunge corrector arranged to give directly the exact volume of a mass of moist air which would measure 100 c.c. when dry and under standard conditions.

The Effect of Temperature on the Total Amount of Gas occluded by Cupric Oxide.

First Series: First Preparation of Cupric Oxide.

		C.c. gas.
1.	1 grm. CuO, heated 1 hour at 300°±, (*a*) gave	0·18
2.	" " " "	0·19
3.	" " " "	0·21
	Average	0·19
4.	1 grm. CuO, heated 4 hours at 500°±, (*b*) gave	0·69
5.	" " " "	0·72
	Average	0·70
6.	1 grm. CuO, heated 1 hour at 830°±, (*c*) gave	0·68
7.	" " " "	0·69
8.	" " " "	0·68
	Average	0·68
9.	1 grm. CuO, heated ½ hour at 870°±, (*d*) gave	0·55
10.	" " at 900°±, (*e*) "	0·08
11.	" " at 950°±, (*f*) "	0·05
12.	" " " "	0·04
	Average	0·05
13.	1 grm. CuO, heated ½ hour at 1100°±, (*g*) gave	0·01(?)

Second Series: Second Preparation of Cupric Oxide.

14.	1 grm. CuO, heated 4 hours at 280°±, (*h*) gave	0·04
15.	" 1 hour at 290°±, (*h*) "	0·12
16.	" 5 hours at 630°±, (*i*) "	0·54
17.	" 3 hours at 830°±, (*j*) "	0·57
18.	" " " "	0·59
19.	" 5 hours " "	0·57
	Average	0·58
20.	1 grm. CuO, heated 20 mins. at 870°±, (*j*) gave	0·42
21.	" 150 " " "	0·23
22.	" " " " "	0·14
23.	1 grm. CuO, heated 2 hours at 950°±, (*j*) gave	0·04
24.	" " " "	0·07
25.	" " " "	0·04
	Average	0·05

(*a*) Mercury thermometer.
(*b*) Plumbic chloride just fused; argentic iodide remained solid.
(*c*) Sodic chloride easily fused; strontic chloride just fused; sodic sulphate remained solid.
(*d*) Sodic sulphate just fused.
(*e*) Sodic sulphate easily fused; higher than last.
(*f*) Baric chloride easily fused; potassic sulphate remained solid.
(*g*) Potassic sulphate fused, as well as the cupric oxide itself.
(*h*) Mercury thermometer.
(*i*) Thallous sulphate just melted.
(*j*) See footnotes to preceding series for criteria regarding temperatures 830°, 870°, and 950°.

These two series of experiments, qualitatively and quantitatively similar to those carried out in 1891, lead to the following conclusions, which are copied verbatim from the paper on the atomic weight of copper:—

"First, *that cupric oxide prepared by the ignition of the oxynitrate after Hampe's method contained between four and five times its volume of occluded gas.*

"Second, *that ignition of the oxide at very bright redness was capable of expelling a portion of this gas. The temperature required was nevertheless considerably above that which Hampe apparently employed.*"

The recent experiments add to these conclusions only greater definiteness. It is now clear that nearly all the gas is retained until a temperature of slightly over 860° is reached, when more than nine-tenths of it is rapidly set free. Somewhat above this point the cupric oxide is itself partly decomposed; and in the neighbourhood of 1000° the mixture of cupric and cuprous oxides fuses first into a mass resembling scoria, and then into a limpid fluid. It is evident that Scott must have used in his muffle a temperature somewhere between 850° and 1000°, for he found on the average 0·055 c.c. of gas per grm. of cupric oxide, while my results obtained by means of temperatures in this neighbourhood average 0·05 c.c. Moreover, some of his material was slightly reduced, but apparently none of it was melted.

It was clearly shown in the previous papers that the low results given by material ignited at temperatures

* Contributions from the Chemical Laboratory of Harvard College; From the *Proceedings of the American Academy of Arts and Sciences*, xxxiii., No. 22; also *American Chemical Journal*, November, 1898.

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below 450° are due to the presence of undecomposed cupric nitrate, which by its decomposition at higher temperatures yields the gas forming the subject of the present discussion.

The fact that prolonged ignition does not affect the amount of gas occluded, may be inferred from the experiments just recorded; but in order to obtain more definite information on this influence of time, a third series of experiments was made.

The Effect of Time of Ignition on the Total Amount of Gas occluded by Cupric Oxide.

Temperature: The Fusing-point of Thallous Sulphate, about 640°.

		C.c. gas.
26.	1 grm. of CuO, after ignition for 10 mins., gave	0·56
27.	" " "	0·57
28.	" " "	0·53
	Average	0·55
29.	1 grm. of CuO, after ignition for 5 hours, gave	0·56
30.	" " "	0·59
	Average	0·57
31.	1 grm. of CuO, after ignition for 20 hours, gave	0·56
32.	" " "	0·59
	Average	0·57

A portion of the last specimen, which had been heated for twenty hours, was further ignited for five hours at about the fusing-point of common salt (about 800°). Upon solution in acid this portion yielded the same amount, 0·59 c.c. of gas. Thus another of the conclusions arrived at in 1892 is confirmed:—

"Third, *that beyond a certain limit the time of ignition makes no important difference.*"

This is true, however, only below 850°. Experiments 20 to 22 show that when the imprisoned gas has once begun to be set free, at temperatures above 850°, the time is an essential factor, and that when sufficient time has been allowed the expulsion of the gas is almost complete. Scott examined only cupric oxide from which he had thus expelled the gas.

In this connection it is interesting to note that Morse and Arbuckle (*Amer. Chem. Journ.*, xx., 195) have recently verified, with apparatus far more elaborate and exact than ours, the results of Rogers and myself, concerning the amount of gas occluded by the oxide of zinc (*Proc. Amer. Acad.*, xxviii., 200). Considering the fact that the manner of preparation of the substance undoubtedly affects the amount of gas retained, the closeness of the agreement is surprising. Only one of their conclusions is different from ours: in their opinion there is no reason to believe that the temperature of ignition of the oxide has any effect on the composition of the occluded gas, while in our experiments the imprisoned oxygen decreased with increasing temperature. The basis of their reasoning is the supposition that the total amount of gas retained is dependent solely upon the temperature; using this total amount as a thermometer, they point out the fact that the smaller amounts of gas obtained in their experiments did not always contain the smaller amounts of oxygen; and hence they conclude that the temperature is not an essential determining cause of the composition of the mixture. In a letter answering some questions about the matter, Professor Morse kindly writes:—"We made every effort to secure constant temperatures for our oxide, giving the closest attention, to that end, to every detail of the firing of the furnace, the fuel, the location of the crucibles," &c. Since this is the case, and I cannot doubt the essential success of their efforts, it seems to me that their results have but little bearing upon the effect of *varying* temperatures on the oxide. The fact that their mixture of gases was by no means constant in composition is better explained by the supposition that some other cause besides the temperature influences the relation of the volumes of oxygen and nitrogen retained, or else that the total amount of the enclosed gases is not a safe measure of the temperature. It will be shown that both of these inferences are correct, and hence that the logic of Morse and Arbuckle's point, correct in itself but unsafe in its premises, falls to the ground.

A careful study of all the data, Morse and Arbuckle's as well as ours, convinced me that, while the two gases must be evolved together, they behave subsequently in quite a different fashion. It is apparent immediately that the oxygen must escape at first much faster than the nitrogen, for the ratio of the two volumes in the nitric anhydride set free must be originally 5 : 2, while the average of Morse and Arbuckle's result showed that less than a fifth of the finally retained mixture consisted of oxygen. Part of the loss might be due to the preliminary formation of lower oxides, and to unequal diffusion, but this cannot account for so great a loss of oxygen. Even nitrous oxide should yield upon decomposition a mixture one-third of the volume of which must consist of oxygen; and the fractional diffusion of this mechanically enclosed mixture should allow the lighter of its two constituents, nitrogen, to escape the more quickly of the two; hence the mixture should contain never less than 33 per cent of oxygen. The same anomaly is even more manifest in the case of cupric oxide, for from this substance nearly all the oxygen soon escapes even at comparatively low temperatures.

Why then does the oxygen escape the more easily of the two gases? This question introduces us at once to the second section of the paper, which deals with the composition of the occluded gases.

The first step toward answering the question is a certain determination of the facts, which have been doubted by Morse and Arbuckle. The three conditions which would be most likely to affect the amount and composition of the gaseous mixture are the temperature of ignition, the time of ignition, and the compactness of the solid material. In order to test the effect of these possible modifying causes experimentally, several series of analyses were made, both with zincic and with cupric oxide.

The zincic oxide was made by heating pure zincic nitrate for a long time at 280°. It was more compact than the cupric oxide, and undoubtedly contained residual traces of nitrate until further ignited.

The Effect of Temperature on the Total Volume of Gas occluded by Zincic Oxide.

First Series: Heated Three Hours.

		C.c. gas.
34.	1 grm. of ZnO, after heating 3 hrs. at 660°± gave	0·365
35.	" " " "	0·380
	Average	0·373
36.	1 grm. of ZnO, after heating 3 hrs. at 750°± gave	0·233
37.	" " " "	0·210
	Average	0·221
38.	1 grm. of ZnO, after heating 3 hrs. at 880°± gave	0·14
39.	" " " "	0·18
	Average	0·16

Second Series: Heated Thirty Minutes.

40.	1 grm. of ZnO, after heating ½ hr. at 750°± gave	0·366
41.	" " " "	0·320
	Average	0·343
42.	1 grm. of ZnO, after heating ½ hr. at 880°± gave	0192
43.	" " " "	0·192
	Average	0·192

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Evidently, other conditions being equal, the total amount of gas retained decreases very considerably as the temperature of ignition is raised. Each one of these specimens of gas was analysed by means of Hempel's apparatus modified for use on a small scale,* with interesting results. The actual volume of *nitrogen* in every grm. of material was found to be almost identical, diminishing only very slightly, if at all, as the temperature increased, and amounting to about 0·14 c.c. Thus the large differences in the total volumes are due almost wholly to *oxygen*, which varied from over 60 per cent in the first average to less than 20 per cent in the third. The small amount of carbon dioxide present was absorbed almost completely by the boiled water over which the gases were collected; hence it need not be considered.† The actual volumes of nitrogen in the five averages were respectively 0·138, 0·133, 0·130, in the first series, and 0·152 and 0·127 in the second series; while the actual amounts of oxygen were respectively 0·235, 0·087, 0·030, in the first series, and 0·191 and 0·065 in the second. No better proof could be desired of the fact that zincic oxide allows its oxygen to depart more easily than its nitrogen. These results are wholly confirmatory of the results of Richards and Rogers already mentioned; but of course they do not explain how Morse and Arbuckle, working at nearly constant temperature, obtained inconstant results. To accomplish this explanation, the other possible causes affecting the retention of gases must be considered.

The Effect of Time of Ignition on the Amount of Gas retained by Zincic Oxide.

First Series: Just above the Melting-point of Thallous Sulphate.

	C.c. gas.
44. 1 grm. of ZnO, heated at 660° for 1 hour, gave	0·46
34. 1 grm. of ZnO, heated at 660° for 3 hours, gave	0·36
35. " " "	0·38
Average	0·37

Second Series: Just above the Melting-point of Potassic Chloride.

45. 1 grm. of ZnO, heated at 750° for 10 mins., gave	0·27
46. 1 grm. of ZnO, heated at 750° for 20 mins., gave	0·35
40. 1 grm. of ZnO, heated at 750°, for 30 mins., gave	0·37
41. " " "	0·32
Average	0·35
47. 1 grm. of ZnO, heated at 750° for 60 mins., gave	0·30
48. " " "	0·32
Average	0·31
36. 1 grm. of ZnO, heated at 750° for 180 mins. gave	0·21
37. " " "	0·25
	0·23

Third Series: Just above the Melting-point of Sodic Sulphate.

49. 1 grm. of ZnO, heated at 880° for 3 mins., gave	0·49
50. 1 grm. of ZnO, heated at 880° for 5 mins., gave	0·35
51. 1 grm. of ZnO, heated at 880° for 12 mins., gave	0·29
52. " " "	0·25
Average	0·27

	C.c. gas.
42. 1 grm. of ZnO, heated at 880 for 30 mins., gave	0·19
43. " " "	0·19
Average	0·19
38. 1 grm. of ZnO, heated at 880° for 180 mins., gave	0·14
39. " " "	0·18
Average	0·16

In each of the series the same fact may be noted,—the fact that continued heating at any one temperature is capable of causing a slow evolution of gas from the oxide. Only in the second of these series is evident an initial increase in the amount of gas, indicating a maximum after less than twenty minutes of heating. This increase, which is manifestly due to the advancing decomposition of the traces of imprisoned nitrate, undoubtedly ceases after an hour's heating at 660°, or after three minutes' heating at 880°; hence it does not appear in the first and third series.

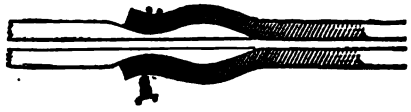

Fig. 2.

The steady loss of gas after this maximum has been attained—a loss increasing with time as well as with increasing temperature in the case of *zincic* oxide—is worthy of further attention, especially because it will be remembered that the amount of gas retained by *cupric* oxide remained almost constant until a very high temperature was reached. Analysis of the several specimens of gas showed at once wherein lay the explanation; for they showed as before that the maximal quantities of gas consisted chiefly of oxygen, while the gas obtained by the last two experiments consisted chiefly of nitrogen. Here again the nitrogen remained nearly constant, only diminishing from 0·20 c.c. at the maxima to about 0·13 c.c. at the minima; while the oxygen diminished in the same samples from 0·21 c.c. to 0·03 c.c.

(To be continued).

CERTAIN ALKALOIDAL PERIODIDES, AND THE VOLUMETRIC ESTIMATION OF ALKALOIDS AS HIGHER PERIODIDES.*

By A. B. PRESCOTT and H. M. GORDIN.

(Continued from p. 19).

Other Atropine Periodides, and Atropine Mercuric Iodides.

Having obtained the enneaiodide of atropine, it was natural to suppose the existence of a heptaiodide, with probability of a complete series from the tri-iodide to the enneaiodide. And in fact in the course of our work we once obtained this heptaiodide. But our efforts to determine the exact conditions necessary for the formation of this body have so far not been successful. Whether additional quantities of atropine will make the precipitate take up more atropine and become a lower periodide we shall try to determine by later experiments. On the other hand, when the order is reversed, and the iodine solution

* The most important modification was the arrangement for connecting pipette to burette. By blowing and drawing down the capillary it may be made to fit so perfectly into the fine rubber tube as to make the loss of small bubbles impossible. The diagram will make the idea clear. (Fig. 2.)

† *Proceedings of the American Academy*, xxviii., 205, 209. In a number of cases where pains was taken to measure the carbon dioxide, its volume never exceeded 3 or 4 per cent, and was usually about 2 per cent.

* The portion of this article which concerns atropine was given in substance in the *Journ. Am. Chem. Soc.*, xx., 329, under the title, "Atropine Periodides and Iodomercurates," by H. M. Gordin and A. B. Prescott (reprints). Also that concerning morphine and opium, except the "Results of Opium Assay," appeared in Kremers' *Pharmaceutical Archives*, June, 1898, i., 121, under the title, "A Volumetric Assay of Opium," by H. M. Gordin and A. B. Prescott (reprints).

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is added to the atropine solution, it is always a lower periodide that is formed; but whether on continued addition of the iodine the precipitate will take up more of it and become a higher periodide we cannot say as yet.

The easiest way to obtain the periodides of atropine is to use chloroform as a solvent. On adding 20 grms. atropine to a warm solution of 30 grms. iodine in chloroform (500 c.c.), the enneaiodide crystallises out very soon in the shape of small, shining, dark green crystals. If these be removed by filtration, the mother-liquor will give several successive crops of the dark blue pentaiodide, and at last a crop of the brownish-red tri-iodide.

Atropine mercuric iodides are best known as products of precipitation of atropine salts by Mayer's reagent, the solution of potassium mercuric iodide (Groves, 1859, *Quar. J. Chem. Soc.*, xi., 97, 188; F. F. Mayer, 1862, *Am. J. Pharm.*, xxxv., 20; Chemical News, vii., 159; viii., 177, 189; Prescott, 1880, *Am. Chem. J.*, ii., 294; xiv., 606). We find that they can be obtained by shaking the alcoholic solution of a periodide with metallic mercury and warming the mixture. Double iodides of atropine and mercury can also be made by mixing theoretical quantities of atropine and iodine, adding a little alcohol and an excess of mercury, slightly warming, and shaking till the colour of iodine disappears. If the higher periodides of atropine be used in the preparation of this double iodide of atropine and mercury, there is always separation of mercurous iodide; but if theoretical quantities of atropine and iodine be used there is no separation of mercurous iodide. The formula of this double iodide of mercury and atropine, as shown by our analysis, seems to be $C_{17}H_{23}NO_3{\cdot}HI{\cdot}HgI_2$. It resembles, in composition, several other double iodides of alkaloids and mercury obtained by Groves by a different method, and agrees in proportion with the strychnine compound, not with the morphine or quinine compound obtained by one of us in 1880 (Prescott, *Am. Chem. J.*, ii., 297). But besides this double iodide we also obtained another having the composition $(Atrop.\ HI)_2{\cdot}HgI_2$. It was made by treating a solution of the $(Atrop.\ HI){\cdot}HgI_2$ in diluted alcohol with an excess of potassium iodide. From the liquid obtained by shaking an alcoholic solution of atropine and iodine with mercury, the monoatropine hydriodide mercuric iodide crystallises out in shining, yellow crystals, melting at 80° to 90° C., difficultly soluble in ether or chloroform, partly soluble in hot water, and very soluble in warm alcohol. The diatropine hydriodide mercuric iodide obtained, as said above, by the action of potassium iodide on the mono compound, crystallises in perfectly white, silky needles, which, on being dried, assume a yellowish tint. They melt at 98° to 99° C., are very easily soluble in warm alcohol, and quite soluble in hot water.

The analysis for mercury and for iodine in these bodies can be made in different ways, but the best results are obtained by a modification of the method of Risse (*Ann. Chem., Liebig*, cvii., 223). The mercury and the iodine are determined in two separate portions. For mercury the substance is dissolved in a little warm alcohol and a little water added; the solution is then acidulated with a few drops of dilute hydrochloric acid, and saturated with hydrogen sulphide. The mercuric sulphide is then dried and weighed in the usual way. For the determination of iodine the substance is treated with a hot solution of potassium hydroxide (1 : 10), diluted with water, filtered, and when completely cold neutralised with acetic acid. The iodine is now precipitated with silver nitrate and nitric acid, and determined as silver iodide in the usual way.

In the following analyses the standard silver nitrate solution was made to correspond with 1 per cent of iodine, and the ammonium thiocyanate solution to correspond, c.c. per c.c., with the silver nitrate solution. The standard solution of iodine contained 1 per cent of iodine, and the sodium thiosulphate solution corresponded, c.c. per c.c., with the iodine solution.

Analyses of the Double Salts of Atropine Hydriodide and Mercuric Iodide.—0·2632 grm. of the monoatropine hydriodide mercuric iodide gave 0·0699 grm. mercuric sulphide, and 0·30445 grm. of the substance gave 0·24785 grm. silver iodide.

	Calculated for $C_{17}H_{23}NO_3{\cdot}HI{\cdot}HgI_2$.	Found.
Mercury	23·03	22·89
Iodine	43·74	43·98

Of the diatropine hydriodide mercuric iodide, 0·1798 grm. gave 0·032 grm. mercuric sulphide, and 0·257 grm. of the substance gave 0·18885 grm. silver iodide.

	Calculated for $(C_{17}H_{23}NO_3{\cdot}HI)_2HgI_2$.	Found.
Mercury	15·58	15·34
Iodine	39·46	39·70

Strychnine Heptaiodide and its Analysis.

The heptaiodide of strychnine is a dark brown powder, hardly soluble in ether, chloroform, or benzol, and requires considerable alcohol for solution. It cannot be re-crystallised, as it is easily decomposed into free iodine and the tri-iodide (a tri-iodide was reported by Tilden in 1865; see Geuther's lists, *loc. cit.*).

The total iodine was determined by silver nitrate after reduction with zinc and ammonia. The additive iodine was estimated after dissolving the periodide in alcohol by titrating with thiosulphate.

For total iodine:—

1. 0·3816 grm. of the periodide gave 0·51345 grm. silver iodide.
2. 0·30625 grm. gave 0·4112 grm. silver iodide.

	Calculated for $C_{21}H_{22}N_2O_2HI{\cdot}I_6$.	Found.
1	72·66	72·70
2	—	72·54

For additive iodine:—

1. 0·1754 grm. of the substance was found to contain 0·109 grm. free iodine.
2. 0·17805 grm. contained 0·111 grm. free iodine.

	Calculated for $C_{21}H_{22}N_2O_2{\cdot}HI{\cdot}I_6$.	Found.
1	62·28	62·14
2	—	62·34

Six atoms iodine coming from the free iodine of the iodopotassium iodide solution, we get the ratio, I_6 to $C_{21}H_{22}N_2O_2$, or 1 of iodine to 0·439 of strychnine absolute. This gives the *decinormal factor* (the value of 1 c.c. of decinormal iodine solution) as 0·0055547 for strychnine.

Brucine Heptaiodide and its Analysis.

This was made according to the general method already given, by pouring a ½ per cent solution of brucine acidulated with hydrochloric acid into a large excess of a 1 per cent solution of iodine. In appearance and solubility it closely resembles the heptaiodide of strychnine, but it exercises a strong reducing action on silver salts, so that its analysis for total iodine is best accomplished by the aid of nitrous acid and bisulphide of carbon as described under the head of morphine tetraiodide and its analysis.

For total iodine:—

1. 0·1916 grm. of the periodide was found to contain 0·13229 grm. total iodine.
2. 0·2395 grm. of the periodide contained 0·16536 grm. total iodine.

	Calculated for $C_{23}H_{26}N_2O_4{\cdot}HI{\cdot}I_6$.	Found.
1	69·21	69·04
2	—	69·04

For additive iodine:—

1. 0·1622 grm. of the substance contained 0·096006 grm. free iodine.
2. 0·192 grm. contained 0·114 grm. free iodine.

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	Calculated for $C_{23}H_{26}N_2O_4 \cdot HI \cdot I_6$.	Found.
1	59·32	59·19
2	—	59·37

For brucine, therefore, the ratio is I_6 to $C_{23}H_{26}N_2O_4$, or 1 of iodine to 0·5179 of anhydrous brucine. And 1 c.c. of strictly decinormal solution of iodine indicates 0·0065530 of brucine, *the decinormal factor*, subjected to trial as stated later.

Morphine Tetraiodide and its Analysis.

Two samples were made. In the first, 1 grm. of morphine dissolved in 200 c.c. acidulated water was added to a solution of 5 grms. iodine and 7½ grms. potassium iodide in 500 c.c. water, the mixture shaken till the supernatant liquid was perfectly clear, and the precipitate washed and dried in vacuum. In the second, 2 grms. iodine and 3 grms. potassium iodide were dissolved in 200 c.c. water, and the solution poured slowly into a solution of morphine containing 3 grms. morphine in 600 c.c. acidulated water. The analysis, as given below, showed that the precipitate in both cases was the same, namely, $C_{17}H_{19}NO_3HI \cdot I_3$. This compound, morphine tetraiodide, was made known by Jörgensen in 1870 (*J. Prakt. Chem.* (2), ii., 437). We find it to be the only periodide formed by morphine under any of the conditions of this precipitation from aqueous solutions.* It is notable that in this periodide the base as a monamine holds an even number of atoms of total iodine. The periodide precipitate of morphine is practically insoluble when the iodine is in excess, though appreciably soluble when the morphine is in excess, as it is in pure water, the more so if strongly acidulated.

In the analysis of the morphine periodide, the precipitate is to be collected and quickly washed with water by the aid of the pump, and then dried in vacuum over sulphuric acid to a constant weight. The additive iodine is readily determined, in a weighed portion, by dissolving in alcohol and titrating with a standard solution of sodium thiosulphate, as stated in previous paragraphs. The total iodine determination in this compound gives special difficulty, as neither the sulphur dioxide nor the powdered zinc, previously used in this laboratory for analytical reduction of periodides, works well with morphine periodide, but the following procedure suffices. The periodide is covered with powdered zinc and stronger water of ammonia and set aside half an hour, the mixture is then heated on the water-bath till all the ammonia is driven off, avoiding loss by spurting. A little water is now added and the mixture boiled about ten minutes. The whole is filtered into a separator of about 500 c.c. capacity, the excess of zinc well washed with hot water, and water added to make 200 or 300 c.c. When perfectly cold the mixture is acidified slightly with very dilute sulphuric acid, then 20 c.c. of carbon disulphide are poured into the separator, and 10 to 12 drops of concentrated sulphuric acid *saturated with nitrous acid* are added. The separator is closed and shaken, and the solution of iodine in carbon disulphide carefully run out upon a wetted filter. Fresh carbon disulphide is added in the separator, and the separation repeated till all the iodine is removed. The iodine is now washed on the filter, first with water, then with a very weak solution of sodium bicarbonate. It is then run into a flask, and 30 c.c. of a solution of sodium bicarbonate, 5 grms. to the litre, are added. Finally the iodine is titrated with the standard solution of sodium thiosulphate. The results were as follows:—

I. Iodine in excess:—

0·2692 grm. gave 0·13 grm. additive iodine, and 0·2732 grm. gave 0·174311 grm. total iodine.

	Calculated for $C_{17}H_{19}NO_3 \cdot HI \cdot I_3$.	Found.
Additive iodine..	48·02	48·29
Total iodine	64·03	63·80

II. Morphine in excess:—

0·3155 grm. were found to contain 0·152832 grm. additive iodine, and 0·2708 grm. contained 0·172076 grm. total iodine.

	Calculated for $C_{17}H_{19}NO_3 \cdot HI \cdot I_3$.	Found.
Additive iodine..	48·02	48·44
Total iodine	64·03	63·54

For morphine the ratio is I_3 to $C_{17}H_{19}NO_3$, or ratio of 379·59 to 284·38, that is 1 of free iodine consumed to 0·74918 of morphine, anhydrous. And 1 c.c. of strictly decinormal solution of iodine corresponds to 0·0094794 grm. of morphine.

Aconitine Heptaiodide (?) and its Analysis.

The alkaloid we used was obtained from Merck, and marked "From Acontum Napellus, crystallised, pure." This periodide was made according to the general plan of obtaining the highest periodide of an alkaloid.

For additive iodine 0·2588 grm. contained 0·126886 grm. free iodine, and 0·1471 grm. contained (by nitrous acid method) 0·082271 grm. total iodine.

	Calculated for $C_{33}H_{45}NO_{12} \cdot HI \cdot I_6$.	Found.
Additive	49·58	49·03
Total	57·85	55·93

We make our calculations upon the aconitine formula of Dunstan (*J. Chem. Soc.*, lxvii., 459). The formula of Freund (*Ber. d. Chem. Ges.*, xxvii., 722), though distinctly different in constitution, gives but slightly different molecular weight. Other proposed formulæ approach the same molecular weight. $C_{34}H_{47}NO_{11} = 643·55$ (Freund). $C_{33}H_{45}NO_{12} = 645·54$ (Dunstan). $C_{33}H_{47}NO_{12} = 647·54$ (Jürgens). $C_{33}H_{43}NO_{12} = 643·54$ (Wright and Luff).

An insufficiency of the aconitine in our hands prevented our making duplicate estimations. With both the higher and the lower periodide, it is to be seen that the total iodine found is somewhat too low for the calculated quantity of this element, calculating for heptaiodide and tri-iodide respectively. The additive iodine in both cases falls below calculation, but not enough below to discredit the formulæ. When we return to these estimations with a larger supply of the alkaloid, we shall find whether the instability of aconitine will prevent constant results in analysis of the higher periodide or not.

Aconitine Tri-iodide (?).

This was made by adding a 1 per cent solution of iodine to an acidulated solution of aconitine, leaving the latter in excess, and re-crystallising the precipitate from alcohol. Thus obtained it forms beautiful brown-red crystals, very soluble in alcohol, insoluble in water, and hardly soluble in ether, benzol, or chloroform. Melting-point, 211—212° C.

For additive iodine:—

0·01773 grm. of the substance contained 0·042352 grm. free iodine.

Calculated for $C_{33}H_{45}NO_{12} \cdot HI \cdot I_6$.	Found.
24·69	23·89

For total iodine by the aid of nitrous acid and bisulphide of carbon, as given under the head of morphine.

0·2111 grm. contained 0·07505 grm. total iodine.

Calculated for $C_{33}H_{45}NO_{12} \cdot HI \cdot I_6$.	Found.
37·03	35·56

(To be continued).

* The present hypothesis of structure of periodides would imply, therefore, that the compound is a dimorphine octaiodide (*Journ. Am. Chem. Soc.*, xvii., 780; xix., 331). A lower periodide of morphine was obtained by evaporation of an alcoholic solution containing excess of morphine, by H. R. Bauer (*Arch. Pharm.* [3], v., 289-309).

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DERIVATIVES OF THE TETRACHLORIDES OF ZIRCONIUM, THORIUM, AND LEAD.*

By J. MERRITT MATTHEWS.

(Continued from p. 17).

D. *Propylamine.*

a. Zirconium Tetrachloride, $ZrCl_4.4C_3H_7NH_2$. — With propylamine, zirconium tetrachloride gave a white compound similar in appearance to the foregoing derivatives.

0·3390 grm. material gave :—
0·4112 grm. silver chloride = 0·1020 grm. chlorine = 30·10 per cent chlorine.
0·0897 grm. zirconium dioxide = 0·0663 grm. zirconium = 19·55 per cent zirconium.

0·6229 grm. material gave :—
0·0892 grm. ammonia = 0·0736 grm. nitrogen = 11·80 per cent nitrogen.

	Calculated for $ZrCl_4.4C_3H_7NH_2$.	Found.
Chlorine	30·30	30·10
Zirconium	19·33	19·55
Nitrogen	11·96	11·80

b. Thorium Tetrachloride, $ThCl_4.4C_3H_7NH_2$.—Propylamine gave a white compound with thorium tetrachloride.

0·2682 grm. material gave :—
0·2537 grm. silver chloride = 0·0628 grm. chlorine = 23·40 per cent chlorine.
0·1167 grm. thorium dioxide = 0·1026 grm. thorium = 38·22 per cent thorium.

0·4213 grm. material gave :—
0·0460 grm. ammonia = 0·0379 grm. nitrogen = 9·01 per cent nitrogen.

	Calculated for $ThCl_4.4C_3H_7NH_2$.	Found.
Chlorine	23·25	23·40
Thorium	38·09	38·22
Nitrogen	9·18	9·01

c. Lead Tetrachloride, $PbCl_4.4C_3H_7NH_2$. — Propylamine at first gave a dark reddish brown precipitate with lead tetrachloride, soon becoming almost white in colour, having a faint yellow tinge.

0·2507 grm. material gave :—
0·2065 grm. silver chloride = 0·0511 grm. chlorine = 20·39 per cent chlorine.
0·2672 grm. material gave :—
0·1195 grm. lead sulphate = 0·0817 grm. lead = 30·56 per cent lead.

0·2817 grm. material gave :—
0·1513 grm. platinum = 0·0217 grm. nitrogen = 7·82 per cent nitrogen.

	Calculated for $PbCl_4.4C_3H_7NH_2$.	Found.
Chlorine	20·73	20·39
Lead	30·22	30·56
Nitrogen	8·28	7·82

E. *Aniline.*

Schiff (*Jahresb. Chem.*, 1863, 412) has obtained a compound of tin tetrachloride with aniline, to which he has given the formula $SnCl_4.4C_6H_5NH_2$; while with titanium tetrachloride Leeds (*Journ. Am. Chem. Soc.*, iii., 145) describes a derivative having the formula $TiCl_4.4C_6H_5NH_2$.

In all of these derivatives the aniline appears to be merely additive. With silicon tetrachloride, however, aniline seems to form a substitution product corresponding to the formula $SiCl_2.(C_6H_5NH)_2$ (Harden, *Journ. Chem. Soc.*, li., 40; Reynolds, *Ibid.*, lv., 474; and Harold, "Thesis," Univ. of Pennsylvania, 1897).

a. Zirconium Tetrachloride, $ZrCl_4.4C_6H_5NH_2$.—On the addition of aniline to the solution of zirconium tetrachloride a greyish flocculent precipitate was produced. This was carefully washed with anhydrous ether until all traces of aniline were removed. It appeared to be stable on drying, and its analysis showed the presence of four molecules of aniline.

I. 0·5382 grm. material gave :—
0·5053 grm. silver chloride = 0·1251 grm. chlorine = 23·25 per cent chlorine.
0·1080 grm. zirconium dioxide = 0·0798 grm. zirconium = 14·83 per cent zirconium.

II. 0·4817 grm. material gave :—
0·4538 grm. silver chloride = 0·1123 grm. chlorine = 23·32 per cent chlorine.
0·0982 grm. zirconium dioxide = 0·0726 grm. zirconium = 15·06 per cent zirconium.

I. 0·5382 grm. material gave :—
0·0600 grm. ammonia = 0·0494 grm. nitrogen = 9·19 per cent nitrogen.

II. 0·6108 grm. material gave :—
0·0678 grm. ammonia = 0·0559 grm. nitrogen = 9·15 per cent nitrogen.

	Calculated for $ZrCl_4.4C_6H_5NH_2$.	Found. I.	Found. II.
Chlorine	23·49	23·25	23·32
Zirconium	14·98	14·83	15·06
Nitrogen	9·27	9·19	9·15

Since analysis would show no difference in the composition of $ZrCl_4.4C_6H_5NH_2$ and a mixture of $ZrCl_2(C_6H_5NH)_2 + 2C_6H_5NH_2.HCl$, the following method was resorted to in order to prove that it was the first and not the second compound which was formed. The substance, after having been completely freed from aniline, was treated with chloroform, in which it proved to be easily and completely soluble, whereas aniline hydrochloride is insoluble in the same reagent, and hence was not present in the compound. Also no substituted chloraniline, $C_6H_4ClNH_2$, could have been formed, as this is soluble in ether, and the existence of no such substance was indicated in the ethereal filtrate. This conclusively proves that the compound is purely additive in nature, and has the formula $ZrCl_4.4C_6H_5NH_2$. This same proof may be used as an argument for the additive character of all the zirconium and thorium derivatives described in this research.

b. Thorium Tetrachloride, $ThCl_4.4C_6H_5NH_2$.—Aniline produced a precipitate slightly grey in colour, and soluble in chloroform. Its analysis indicated a formula in correspondence with that of the zirconium derivative.

0·2536 grm. material gave :—
0·1940 grm. silver chloride = 0·0479 grm. chlorine = 18·89 per cent chlorine.
0·0906 grm. thorium dioxide = 0·0796 grm. thorium = 31·39 per cent thorium.

0·5536 grm. material gave :—
0·0488 grm. ammonia = 0·0402 grm. nitrogen = 7·41 per cent nitrogen.

	Calculated for $ThCl_4.4C_6H_5NH_2$.	Found.
Chlorine	19·02	18·89
Thorium	31·15	31·39
Nitrogen	7·61	7·41

c. Lead Tetrachloride, $PbCl_4.3C_6H_5NH_2$.—Aniline gave a dark green stable compound with lead tetrachloride in dilute solution. A more concentrated solution of the lead salt reacts very violently with aniline, probably giving rise to the same chlorinated products as tin tetrachloride, such as violaniline, mauvaniline, rosaniline, and triphenylendiamine blue (Girard and Pabst, *Bull. Soc. Chim.*, xxxiv., 33). The dark green compound analysed for three molecules of aniline.

* Contribution from the John Harrison Laboratory of Chemistry. From the *Journal of the American Chemical Society*, xx., No. 11. From author's thesis for the Degree of Doctor of Philosophy.

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0·2104 grm. material gave :—
0·1950 grm. silver chloride = 0·0483 grm. chlorine = 22·94 per cent chlorine.
0·2042 grm. material gave :—
0·0963 grm. lead sulphate = 0·0658 grm. lead = 32·22 per cent lead.

0·4012 grm. material gave :—
0·1929 grm. platinum = 0·0277 grm. nitrogen = 6·90 per cent nitrogen.

	Calculated for $PbCl_4 \cdot 3C_6H_5NH_2$.	Found.
Chlorine	22·61	22·94
Lead	32·96	32·22
Nitrogen	6·69	6·90

F. *Toluidine.*

a. Zirconium Tetrachloride, $ZrCl_4 \cdot 4C_6H_4CH_3NH_2$.—As aniline gave a derivative with zirconium tetrachloride, toluidine was also tried with like result. Analysis indicated that this compound contained four molecules of toluidine, showing it to be analogous to the aniline derivative.

0·3772 grm. material gave :—
0·3240 grm. silver chloride = 0·0802 grm. chlorine = 21·26 per cent chlorine.
0·0694 grm. zirconium dioxide = 0·0512 grm. zirconium = 13·60 per cent zirconium.

0·4296 grm. material gave :—
0·0456 grm. ammonia = 0·0376 grm. nitrogen = 8 74 per cent nitrogen.

	Calculated for $ZrCl_4 \cdot 4C_6H_4CH_3NH_2$.	Found.
Chlorine	21·50	21·26
Zirconium	13·72	13·60
Nitrogen	8·48	8·74

b. Thorium Tetrachloride, $ThCl_4 \cdot 3C_6H_4CH_3NH_2$.—This was a greenish white precipitate and showed a departure from the other derivatives and from its analogous zirconium compound in that it only contained three molecules of the base.

0·5012 grm. material gave :—
0·4074 grm. silver chloride = 0·1008 grm. chlorine = 20·12 per cent chlorine.
0·1940 grm. thorium dioxide = 0·1705 grm. thorium = 34·01 per cent thorium.

0·7500 grm. material gave :—
0·0526 grm. ammonia = 0·0433 grm. nitrogen = 5·78 per cent nitrogen.

	Calculated for $ThCl_4 \cdot 3C_6H_4CH_3NH_2$.	Found.
Chlorine	20·41	20·12
Thorium	33·44	34·01
Nitrogen	6·04	5·78

c. Lead Tetrachloride.—With toluidine no additive product could be obtained even by using quite dilute solutions of lead tetrachloride, as the amine was decomposed, giving a deep purple solution. Hence lead tetrachloride evidently has about the same action on toluidine as bleaching lime or tin tetrachloride.

G. *Pyridine.*

As pyridine and quinoline are strong bases, and as they may be considered tertiary amines, it was thought probable that these reagents would form derivatives with the tetrachlorides in a manner similar to aniline and toluidine. Experiment proved this surmise to be a correct one, as a compound was formed in both instances. It may be stated that Classen and Zahorski (*Zeit. Anorg. Chem.*, iv., 100) have obtained compounds of lead tetrachloride with the hydrochlorides of pyridine and quinoline, and they are described as additive products. Goebbles (*Ber. d. Chem. Ges.*, xxviii., 792) has also obtained compounds of lead tetrachloride with the salts of such complex organic bases as picoline, lutidine, and collidine.

The compounds of zirconium and thorium tetrachlorides with pyridine and quinoline are light grey to brown flocculent precipitates. Unlike the derivatives with the preceding amines, they appeared to be rather unstable in moist air, in consequence of which considerable difficulty was experienced in obtaining suitable portions for analysis, as the compounds had to be preserved under anhydrous ether.

a. Zirconium Tetrachloride, $ZrCl_4 \cdot 2C_5H_5N$.—The best analysis that could be obtained for the pyridine derivative approximated to a formula containing two molecules of the base.

0·5420 grm. material gave :—
0·7805 grm. silver chloride = 0·1932 grm. chlorine = 35·64 per cent chlorine.
0·1758 grm. zirconium dioxide = 0·1299 grm. zirconium = 23·97 per cent zirconium.
0·6118 grm. material gave :—
0·0506 grm. ammonia = 0·0417 grm. nitrogen = 6·83 per cent nitrogen.

	Calculated for $ZrCl_4 \cdot 2C_5H_5N$.	Found.
Chlorine	36·35	35·64
Zirconium	23·19	23·97
Nitrogen	7·18	6·83

b. Thorium Tetrachloride, $ThCl_4 \cdot C_5H_5N$.—0·5002 grm. material gave :—
0·6270 grm. silver chloride = 0·1552 grm. chlorine = 31·02 per cent chlorine.
0·2939 grm. thorium dioxide = 0·2583 grm. thorium = 51·64 per cent thorium.
0·4107 grm. material gave :—
0·0126 grm. ammonia = 0·0104 grm. nitrogen = 2·53 per cent nitrogen.

	Calculated for $ThCl_4 \cdot C_5H_5N$.	Found.
Chlorine	31·30	31·02
Thorium	51·28	51·64
Nitrogen	3·09	2·53

c. Lead Tetrachloride, $PbCl_4 \cdot 2C_5H_5N$.—Pyridine gave a pale yellow precipitate with lead tetrachloride of much greater stability than the foregoing compounds.
0·2506 grm. material gave :—
0·2780 grm. silver chloride = 0·0688 grm. chlorine = 27·46 per cent chlorine.
0·3125 grm. material gave :—
0·1842 grm. lead sulphate = 0·1258 grm. lead = 40·26 per cent lead.
0·3062 grm. material gave :—
0·1112 grm. platinum = 0·0161 grm. nitrogen = 5·21 per cent nitrogen.

	Calculated for $PbCl_4 \cdot 2C_5H_5N$.	Found.
Chlorine	28·01	27·46
Lead	40·83	40·26
Nitrogen	5·52	5·21

(To be continued).

Messrs. John J. Griffin and Sons, Ltd., the well-known makers of scientific instruments, who have removed from their old premises in Garrick Street to Sardinia Street, Lincoln's Inn Fields, have sent us their Catalogue —Part III., Magnetism, Electricity, and Galvanism. The list includes some of the latest pieces of apparatus, as well as some almost obsolete. We note several forms of Wimshurst electrical machines, Kelvin's galvanometers, Ayrton weather instruments, Röntgen ray outfits, telephones, arc lamps, and electric furnaces. The illustrations are good and numerous, and the catalogue is likely to prove of great use to any having the responsibility of schools and technical institutions, especially those in country places.

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NOTICES OF BOOKS.

A Manual of Chemical Analysis, Qualitative and Quantitative. By G. S. Newth, F.I.C., F.C.S. London, New York, and Bombay: Longmans, Green, and Co. 1898. Pp. 462.

The volume now before us treats the subject of both qualitative and quantitative analysis in a clear and comprehensive manner. Beginning with the simplest reactions in both the wet and dry ways, the student is led on through simple tests to group analysis, after which the rare earths and metals are dealt with. When this branch has been thoroughly mastered, the principles and practice of quantitative analysis are fully explained, both gravimetrically and volumetrically. A very good plan has been adopted in first giving an "epitome of process," and then proceeding to the more detailed instructions for carrying out whatever analysis or process is being dealt with.

The book is very well adapted for both class and laboratory work, and should rank among the standard text-books of science.

Practical Pharmacy: an Account of the Methods of Manufacturing and Dispensing Pharmaceutical Preparations, with a Chapter on the Analysis of Urine. By E. W. Lucas, F.C.S. With 283 Illustrations. Pp. 528. London: J. and A. Churchill. 1898.

Although a certain portion of this work is devoted to manufacturing processes, the bulk of it deals with the ordinary method and routine of pharmacy and dispensing. It is essentially a book for students, beginning as it does with the simplest chemical instruction. There is, however, too great a tendency in such books now-a-days to assume that the reader or student knows nothing of the subject he is taking up as a profession; we very much doubt if the early chapters are ever read, filled as they are with descriptions and illustrations of the simplest and commonest articles used in chemical laboratories. Tables of weights and measures, and such like information, are supposed to be learnt at school, and a quarter-page illustration of copper gallon and quart measures surely seems unnecessary.

The book is divided into six parts, comprising general processes and descriptions of apparatus, pharmacopœial preparations, dispensing, pharmaceutical tests, volumetric and gravimetric analysis, tables, and a chapter on the analysis of urine, in which will be found a number of excellent enlarged microscopic plates.

After the preliminaries are got over the book will be found to be sound, and clearly written, and will be of value to the student. There is a copious index of eleven pages.

CORRESPONDENCE.

THE ORIGIN OF THE GASES EVOLVED ON HEATING MINERAL SUBSTANCES, METEORITES, &c.

To the Editor of the Chemical News.

Sir,—In an interesting paper on the above subject recently read before the Royal Society, and published in the Chemical News (lxxviii., p. 305), Dr. M. W. Travers discusses the source of the gases given off on heating meteorites. The conclusion he arrives at is thus stated in his own words:—"It would appear then that the gases produced by the action of heat upon meteorites are not present as such, but are the products of decomposition of their non-gaseous constituents. It is therefore impossible to draw conclusions as to the former history of a meteorite from the nature of the gases which it gives on heating."

From the tenour of some of the remarks made by Dr Travers, I judge that he is not aware that the same conclusion has been reached before. May I therefore draw attention to a paper in the *Philosophical Magazine* of June, 1883, on the "Regenerative Theory of Solar Action"; where, in discussing the well-known speculation of the late Sir William Siemens, I have considered the question as to whether the composition of the gases found occluded in meteorites supports the view of the existence of an atmosphere rich, in hydrogen, existing in space. After quoting the experimental results, and explaining how the gases can be formed from the substances contained in the meteorites themselves, I conclude "that they afford us no insight into the composition of the supposed interplanetary atmosphere."—I am, &c.,

Ernest H. Cook.

The Clifton Laboratory,
January 10, 1899.

ESTIMATION OF LEAD.

To the Editor of the Chemical News.

Sir,—In reply to the second question of your querist "Cox" (Chem. News, lxxix., 12), may I say that the estimation of lead, outlined in the Appendix of Mr. Brearley's paper on the "Estimation of Molybdenum Compounds," could be readily adapted to the determination of lead in iron and calcium compounds. As it is very unlikely that any satisfactory precipitation of lead molybdate can be made in the presence of iron, that element would need to be separated. Either alkaline acetates or soda hydrate could, I believe, be used to this end.

The very large number of elements in whose presence molybdenum has been shown to be accurately precipitable as lead molybdate by a lead salt, at once suggests the converse operation of estimating lead in their presence. If in this converse operation there can be added tin, antimony, and bismuth to those elements Mr. Brearley has already experimented with, then the method would be a valuable one for the examination of the numerous commercial lead alloys.

This line of investigation I have been for some time engaged upon, and hope shortly to publish the results, amongst others, of special interest to "Cox."—I am, &c.,

R. Leffler.

The Laboratory,
Thos. Firth and Sons, Lim., Sheffield.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

Note.—All degrees of temperature are Centigrade unless otherwise expressed.

Comptes Rendus Hebdomadaires des Séances, de l'Académie des Sciences. Vol. cxxvii., No. 21, November 21, 1898.

Relation between Luminous and Chemical Energy and Displacement of the Halogen Elements by Oxygen.—M. Berthelot.—The author examines—(1) The action of iodine and oxygen, finding that iodic anhydride and also iodic hydrate are slowly decomposed into their elements under the influence of solar light at ordinary temperatures, the effect of the light being the same as that of heat, if the temperature of the substance is raised in the absence of light. This action, however, is not reversible, iodine and oxygen not combining at any known temperature. This reaction proves, what the author has also studied experimentally, that solar light does not in any degree change ordinary oxygen into ozone. For, this being the case, iodine must be at once oxidised. The same experiments were repeated in the presence of water

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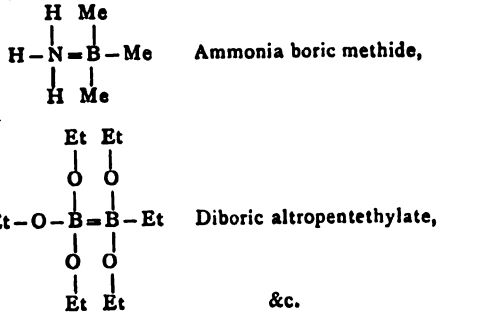
with again negative results. (2) The action of bromine and oxygen, finding that bromine or chlorine and free oxygen do not combine. However, chlorine and even bromine decompose water in the cold, giving off oxygen. The action of bromine on water is almost imperceptible in darkness, but quite perceptible under the influence of solar light. Reciprocally bromic acid is decomposed by oxygen at a high temperature.

Atomicity of Boron.—E. Frankland.—Referring to M. Copaux's paper on the new compound of boron which indicates its pentatomicity, the author states that in 1876 he obtained with boric methide and boric ethide a number of compounds, for which were suggested the formulæ—



which confirms the pentatomicity of boron and its power of uniting with itself in the same manner as carbon.

No. 22, November 28, 1898.

Condensed Oxides of the Rare Earths.—G. Wyrouboff and A. Verneuil.—The authors have examined the oxides of cerium with a view to replacing the confused notion of basic salts by the exact theory of successive condensation of the oxide. It appears much more rational to consider the combinations as neutral or acid salts of an oxide, which in condensing necessarily changes its valency. One of the most characteristic properties of the rare earths is their faculty of polymerising, under the influence of the most varied causes, and also their tendency to form among themselves very stable compounds of complex oxides, which properties naturally are expected from the above theory.

Observations on the Spectra of Aluminium, Tellurium, and Selenium.—A. de Gramont.—The author finds that certain lines in the spark spectrum of aluminium, tellurium, and selenium, as measured by Thalén and by himself in former papers, are due to impurities. He has obtained aluminium in a greater state of purity than that in which it has been obtained before, and from a study of the spectrum attributes Thalén's lines 637·13, 634·48, and 505·66, to silicon. In tellurium and selenium the lines 521·7, 515·3, 510·5 he attributes to copper.

Aromatic Urethanes of Tetrahydroquinoline.—MM. Cazeneuve and Moreau.—The action of secondary bases of the aromatic series on phenolic carbonates gives rise to urethanes, as shown by the derivatives of piperidine, conicine, piperazine, before described. The action of tetrahydroquinoline confirmed this reaction, which appears to be general for bodies of this type. An excess of base was used. On heating for two hours to the boiling-point 4 molecules of tetrahydroquinoline with 1 molecule of phenol carbonate, the following urethanes were obtained:—Phenyl, orthochlorphenyl, guaiacol, and α- and β-naphthol. These are all white bodies, very stable, fusible, and boiling almost without decomposition at about 300°.

Action of Potash on Oxynitrocellulose.—Léo Vignon.—Oxycellulose having been nitrated by a mixture of 1 part of H_2SO_4 and 3 parts of HNO_3, the oxynitrocellulose obtained was mixed with KOH, and the temperature raised to 45° for seven minutes. At the same time the oxynitrocellulose dissolved with a slight evolution of gas giving a brown liquid. This solution was cooled to 0°, and neutralised by acetic acid; it then became nearly colourless, and on a current of H_2S being passed through at the ordinary temperature, oxides of nitrogen were evolved, sulphur deposited, and a brown liquid obtained. This liquid, to which was added a solution of acetic acid and phenyl-hydrazine, was warmed to 80°, resulting in the formation of a crystalline precipitate: 100 grms. of oxynitrocellulose yielded 8 grms. of this precipitate, which consists of small yellow crystals. Analysis gave the following percentages:—C 64·40, N 19·33, H 5·40, O 11·87. The melting-point, 204, is identical with that of the osazone of oxypyruvic acid, and the analysis gives the same composition. Hence oxypyruvic acid,—

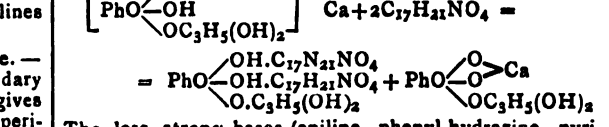
$$OH.CH_2CO.CO.OH = C_3H_4O_4$$

is the result of treating oxynitrocellulose with potash.

Journal de Pharmacie et de Chimie, vol. viii., No. 4.

Researches on Urinary Phosphorus.—L. Jolly.—These researches show that the urinary phosphorus which escapes estimation by the ordinary methods used for phosphoric acid is not incompletely oxidised phosphorus, or phosphoglyceric acid, according to one hypothesis which has been put forward, but simply phosphoric acid combined with metallic bases, again intimately associated with nitrogenous matter, an association which resists the action of digestives, and of the intra-organic oxidants.

The Organic Phosphoglycerates.—MM. Adrian and Trillat.—The preparation of the organic phosphoglycerates (of cocaine, quinine, phenyl-hydrazine, &c.) is as follows:—A solution of a neutral glycerophosphate of lime is treated with dilute sulphuric acid until it is just acid to heliantine, and is then brought back to neutrality with a few drops of neutral glycerophosphate; heat and filter off the calcic sulphate thus precipitated. After having added the base until the reaction is alkaline, and then a great excess of alcohol, the whole must be again heated for a few minutes, and filtered with a filter-pump to separate the precipitated glycerophosphate of lime; the solution must be concentrated at as low a temperature as possible, and desiccated *in vacuo* over sulphuric acid; the residue is taken up with a little water, and shaken up several times with ether, to remove all excess of the base; the aqueous solution is again evaporated down, and the residue triturated with strong alcohol. The unprecipitated phosphoglycerate of lime remains in suspension; the residue soluble in alcohol is finally dried at 50° to 60°. The strong bases only (quinine and cocaine) seem able to completely displace the lime of the acid phosphoglycerate according to the equation—



The less strong bases (aniline, phenyl-hydrazine, pyridine, &c.) precipitate a certain amount of the neutral phosphoglycerate of lime, but the residue from the filtrate contains a considerable proportion of a body either insoluble or only slightly soluble in alcohol: it has the formula—

The Decolouration of Wines by means of Salts of Manganese.—P. Jacob.—Not suitable for abstraction.

The Purification of Potable Waters.—P. Guichard.—The author points out that the water of the River Vanne contains 700 microbes per c.c. when it arrives in Paris, and that this number has increased to 212,000 by

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the time it reaches the consumer. He therefore thinks that the purification of the water should be undertaken individually by the use of filters, the merits of some of which he discusses.

The Coagulation of Albumen.—G. Halphen.—From experiments made, and here described, the author concludes that some ammonium salts, such as the citrate and hydrochlorate, favour the separation of albumen; that the soda set free at the moment of coagulation displaces the alkali of the ammonia salt, thus creating a more favourable medium for coagulation; that the coagulation of albumèn is complete in the presence of citrate or of ammoniacal salts; and that operations carried out for the purpose of estimating the albumen are much more exact and are less troublesome when ammonia salts are used.

MEETINGS FOR THE WEEK.

MONDAY, 23rd.—Society of Arts, 8 (Cantor Lectures). "Bacterial Purification of Sewage," by Dr. Samuel Rideal.

TUESDAY, 24th.—Royal Institution, 3. "The Morphology of the Mollusca," by Prof. E. Ray Lankester, M.A., LL.D.

—— Society of Arts, 4.30. "Rhodesia and its Mines in 1898," by W. Fischer Wilkinson, F.G.S.

WEDNESDAY, 25th.—Society of Arts, 8. "Tuberculosis in Animals," by W. Hunting.

THURSDAY, 26th.—Royal Institution, 3. "Tibet and the Tibetans," by A. Henry Savage Landor.

FRIDAY, 27th.—Royal Institution, 9. "Epitaphs," by Sir Mountstuart E. Grant Duff, F.R.S.

—— Physical, 5. "On the Equivalent Resistance and Inductance of a Wire to an Oscillatory Discharge," by E. H. Barton, D.Sc. Exhibition of (*a*) Dephlegmator, (*b*) A Temperature Tell-Tale, by R. Appleyard. "On the Volume Changes accompanying Solution," by T. H. Littlewood.

SATURDAY, 28th.—Royal Institution, 3. "Tschaikowsky" (with Musical Illustrations), by Sir Alexander C. Mackenzie, Mus. Doc.

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THE CHEMICAL NEWS.

VOL. LXXIX., No. 2044.

THE PREPARATION AND SOME OF THE PROPERTIES OF PURE ARGON.*

By WILLIAM RAMSAY, F.R.S., and MORRIS W. TRAVERS.

In the memoir on argon, and new constituent of the atmosphere (*Phil. Trans.*, A, Part I., 1895, p. 187), by Lord Rayleigh and one of us, reasons are adduced on pages 235 and 236 in favour of the supposition that argon is an element, or a mixture of elements; and on page 236 the following words occur:—"There is evidence both for and against the hypothesis that argon is a mixture, for, owing to Mr. Crookes's observations of the dual character of its spectrum; against, because of Professor Olszewski's statement that it has a definite melting-point, a definite boiling-point, and a definite critical temperature and pressure; and because on compressing the gas in presence of its liquid, pressure remains sensibly constant until all gas has condensed to liquid. The latter experiments are the well known criteria of a pure substance; the former is not known with certainty to be characteristic of a mixture." And on pages 257-259 of the same volume, it is shown by Professor Sydney Young and one of us that the ratios between the boiling-points of argon and benzene, argon and alcohol, and argon and oxygen on the absolute scale are such that it is possible to compute the boiling-points of argon at different pressures with very considerable accuracy. We therefore draw the conclusion:—"It is hardly likely, though not impossible, that so good an agreement would be obtained with a mixture or an impure substance. It is, at any rate, certain that a distinct want of agreement would have shown that argon was not a definite, pure substance, and the results may be taken as affording additional confirmation of the conclusion that argon is a definite, hitherto unknown constituent of the atmosphere, and that it has been isolated in a state very closely approaching to purity."

The density of a sample of argon prepared by means of magnesium was found by one of us to be 19·941 (O=16); and a much larger preparation by Lord Rayleigh, obtained by exposing a mixture of air and oxygen to an electric flame in presence of caustic soda, possessed the density 19·94. Supposing argon to be a simple substance, and not a mixture, the atomic weight would therefore be 39·88. An attempt was made by Dr. J. Norman Collie and one of us to effect a separation of argon into a light and a heavy portion passing by diffusion, but without definite results. While the density of the portion passing first through the pipe-clay septum was 19·93, that of the last portions was 20·01. We remarked on these figures in the following terms:—"These numbers show that no important separation has been effected. The difference in density of the two portions may possibly be attributed to experimental error. . . . As it stands, the difference is an extremely minute one, and it may, we think, be taken that any separation of argon, if effected at all, is very imperfect."

It thus remained uncertain whether argon was a mixture or not, although the balance of evidence went against the supposition.

When helium was discovered in 1895 a new light was thrown on the question. Its density, determined by Ramsay, and independently by Langlet, closely approximates to 2·0. Experiments, in conjunction with Dr. Collie, and subsequently by ourselves, showed that no great difference in density could be brought about by fractional diffusion, and, indeed, the latter revealed no impurity, except traces of argon. On grounds similar to those from which a corresponding conclusion for argon was drawn, the atomic weight of helium must be somewhat below 4·0. The difference between the atomic weights of helium and argon is consequently about 36; and this is approximately the difference between the atomic weights of manganese and fluorine (36), chromium and oxygen (36·3), vanadium and nitrogen (37·4), and titanium and carbon (36·4). But between each of these pairs of elements there exists another, exceeding in atomic weight the lower member of each pair by approximately 16. It was therefore to be expected that another element should exist with atomic weight about 20, and on the assumption that, like helium and argon, it too would be a monatomic gas, its density would be 10. It was with the object of attempting to discover this unknown gas that the experiments on the fractional diffusion of helium were made, and the gases evolved on heating some fifty minerals were investigated in order to find out whether a new spectrum could be observed, but with negative results. Seven meteorites were also examined, as well as six mineral waters, but no new lines could be found. Sixteen of the minerals, two of the mineral waters, and one of the meteorites were proved to contain helium, but if the gases extracted from them contained any gas other than helium or a trace of argon, it must have been in quantity too minute to have revealed itself to the spectroscope.

The gas which we were in search of was ultimately found in argon. The argon, amounting to about 15 litres, was prepared by means of apparatus, of which a description is given in the sequel. From the air employed in a liquid state for the purpose of liquefying and fractionally distilling the argon, two other elementary gases have been obtained, besides one yielding the "Swan" spectrum. A preliminary account of all these gases has already been given in the *Proceedings of the Royal Society* under the names of "Neon," or "new," "Krypton," or "hidden," and "Metargon," and at the meeting of the British Association at Bristol, the discovery of "Xenon" or "the stranger" was announced. The removal of these gases from argon has put us in possession of pure argon, and the present paper deals with some of its properties.

The Properties of Pure Argon.

In order to prepare 15 litres of argon, it is necessary to deal with about 1500 litres of atmospheric air, of which approximately 1200 litres consist of a mixture of nitrogen and argon. To absorb the nitrogen contained in this quantity of gas by conversion into nitride, 4 kilogrms. of magnesium would be required theoretically, but in order to cover loss through leakage and incomplete action, 5 kilogrms. of the metal are employed. The absorption of the oxygen and nitrogen was conducted in three stages. In the first, the oxygen was removed by means of metallic copper; in the second, the nitrogen was passed twice over metallic magnesium; and in the third, the gas, now rich in argon, was finally freed from nitrogen and hydrogen by passage over a mixture of anhydrous lime and magnesium powder heated to a red heat, and subsequently over red-hot copper oxide. The apparatus employed is shown in detail in the annexed figure.

It was of course necessary to confine the gas over water between the successive stages of purification, and finally to store the gaseous argon in the same way. On account of the considerable solubility of argon in water, this would have entailed no small loss if the quantity of water with which it had been brought into contact had been large. We consequently decided to make use of gas-holders of the gasometer type, in which the water was contained in an annular space of small capacity. Balance weights were attached to cords passing over pulleys, and served to relieve the pressure on the gas due to the weight of the gasometer. As the volume of the gas decreased after each successive stage, the four gas-holders employed were of

* A Paper read before the Royal Society, December 15, 1898.

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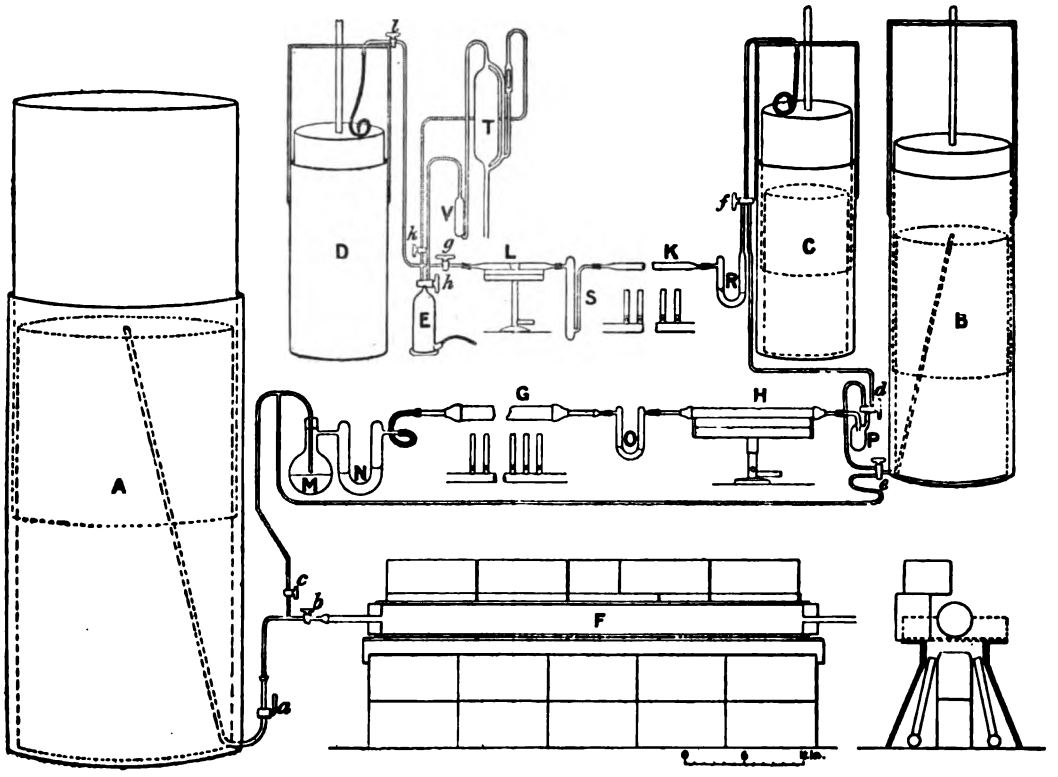

FIG. 2.

different sizes; the capacity of A was about 180 litres; that of B, 27 litres; and of C and D, each 18 litres.

Atmospheric nitrogen was obtained by drawing air, freed from carbon dioxide by passage through caustic soda solution, over heated metallic copper. A large iron tube F, 3 feet 6 inches long, and 3·5 inches in diameter, containing 25 lbs. of scrap copper, was connected with the gas-holder A; the tube was heated in a long fire-brick trough during these experiments, but a gas-furnace is shown in the figure, which has now been substituted for the more primitive arrangement.

The time required to fill the gas-holder was usually about five hours, and it was found, on analysis of the gas, that one single operation sufficed for the complete removal of all oxygen. The oxidised copper was reduced between each operation by means of coal-gas.

By closing the stop-cock *b*, and opening the stop-cock *c*, the gas-holder A could be placed in communication with the apparatus in which the preliminary absorption of nitrogen took place. By placing weights on the top of the gas-holder, the nitrogen was driven through the vessel M and the U-tube N, both of which contained strong sulphuric acid, into the tube G, which contained magnesium. This tube was a piece of steam-barrel, 1·5 inches in diameter, connected at each end by a reducing socket with an iron tube, 0·25 inch in diameter. The tube contained 250 grms. of magnesium, cut into coarse shavings in a shaping machine; the magnesium was not pressed very tightly into the tube. Since after each operation it was necessary to remove the sockets in order to clear the tube, the joints were luted with red lead, and the tube was made of sufficient length to project about 3 inches at each end of the furnace.

The greater part of the nitride was generally removed by using an iron rod, and the remainder by means of water, which converted it into the hydroxide. The tube was raised to a bright red heat before connecting it with the U-tube O, in order to allow the greater part of the hydrogen occluded by the magnesium to escape. The absorption of the nitrogen, which was indicated by the rate of flow of the gas through the U-tubes N and O, was maintained briskly until practically the whole of the magnesium was converted into nitride; the volume of the gas absorbed was equivalent to half the capacity of the large gas-holder.

The gas, after leaving the U-tube O, passed through a second iron tube H containing copper oxide; next, through the vessel P, in which water condensed; and it finally collected in the gasometer B. That which passed during the first stages of the process consisted of nitrogen containing much argon, but towards the end of the operation the argon became much diluted, until finally the gas which passed through the U-tube O consisted almost entirely of atmospheric nitrogen. The tube G was then replaced by another containing a fresh supply of magnesium.

The tap *e* was then closed, and the taps *d* and *e* turned, so that the gas in the gasometer B could be made to flow through the magnesium and copper oxide tubes into the gasometer C. In this process its volume was very much reduced, and the gas which collected in C probably contained as much as 25 per cent of argon. When the whole of the gas had been expelled from B, the taps *d* and *e* were again turned, and atmospheric nitrogen was allowed to flow through the magnesium tube, as in the first stage of this operation.

When the gasometer C had become full of the mixture of nitrogen and argon, as it did at the end of every third or fourth operation, it became necessary to reduce its volume by further absorption of nitrogen. The method employed, which was first described by Maquenne (*Compt. Rend.*, 1895, vol. cxxi., p. 1147), consisted in passing the gas through a hard glass tube containing a mixture of magnesium powder and lime, heated to a dull red heat in

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a combustion furnace. The lime was obtained by thoroughly calcining precipitated chalk in a muffle. The nitrogen continued to be completely absorbed as long as calcium remained unattacked, so that the product of this operation consisted of pure argon. The gas issuing from the calcium tube passed through a tube S, containing soda-lime, and over copper oxide in the tube L, on its way to the gasometer D. Since at the end of the operation the system of tubes between the gas-holders C and D contained argon, in order to avoid loss, the circuit was placed in communication with a Töpler pump T, through the stop-cock *k*. The space between the stop-cocks *l* and *f* was exhausted at the commencement of the operation, the exhaustion being continued till the greater part of the hydrogen, which is always evolved when a mixture of magnesium and lime is heated, had been given off.

When it was necessary to suspend operations, the taps *l* and *f* were closed, the tap *k* was opened, and the argon was taken into the pump and delivered into the vessel V, which covered the upturned end of the capillary tube of the pump. From V the argon could be drawn into the small gas-holder E, which contained mercury, and which could also be placed in communication with the system through which the gas passed on its way from C to D.

These operations were repeated until the gasholder D contained about 15 litres of argon. The whole of this argon was then liquefied in an apparatus of which Fig. 2

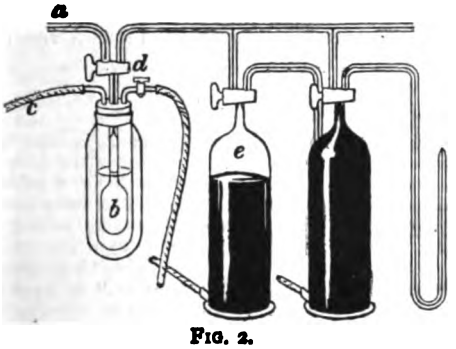

Fig. 2.

is a representation. The argon entered through the tube *a* into the bulb *b*, of some 25 c.c. capacity, surrounded by liquid air contained in a double-walled vacuum jacket. The air was made to boil under a low pressure of a few centimetres of mercury by means of a Fleuss pump attached to the tube *c*. The argon rapidly and completely liquefied to a colourless mobile liquid; it showed no absorption spectrum. Its volume was about 17·4 c.c. By turning the tap *d* it was placed in communication with the first of the series of mercury gasholders, *e*; the reservoir was then lowered so as to remove the lower-boiling portions of the liquid. During this distillation, which took place at constant temperature, the pressure on the boiling air was kept as low as possible. This gas subsequently turned out to be rich in neon, and to contain helium (*Roy. Soc. Proc.*, lxiii., 437). The remainder of the argon boiled back into the gasometer until the last few drops were left; the residue solidified, and finally gave a gas to which we gave the name metargon; it was collected in mercury gasholders (*loc. cit.*, p. 439). As will be subsequently shown, the krypton and xenon in this quantity of argon are too minute for detection. A similar operation for the purpose of separating the lighter as well as the heavier constituents was afterwards repeated three times, the middle portion of argon being always returned to the gasholder D (Fig. 1). A fourth liquefaction was carried out in which six mercury gasholders were filled with six separate fractions of argon, each taken after each successive fifth of the total argon had evaporated. These fractions were next purified from any nitrogen accidentally present by sparking with oxygen over caustic potash. After the removal of the oxygen the density was determined.

(To be continued).

DETERMINATION OF THE IODINE VALUE FOR FATTY MATTERS.

By C. ASCHMANN.

In the analysis of a fatty body, Hübl's method may give very valuable indications as to the purity of the substance under examination. Numerous modifications have been introduced to this method with a view to render it sufficiently exact, but this end has not yet been achieved.

To obtain concordant values for the iodine for one and the same fat or oil, it is necessary for the titration value of the iodised solution to remain constant, and that the duration of the reaction, the temperature, and the method of agitation should be identical in every experiment. As we well know, Hübl's solution is very unstable. Waller has removed this difficulty by suppressing it entirely. Now, I have succeeded in preparing a chloro-iodised solution which gives excellent results, and of which the value remains *constant*. The strength of my solution is such that it gives nearly the same figures as Hübl's freshly-prepared solution; these figures, however, relate to the volume, and not the weight of the fatty body. I have found, in fact, that weighing—and, above all, pouring oils from one glass to another—easily leads to errors. On the other hand, measurement by volume, as I propose, is simple and very exact.

Preparation of the Chloro-iodised Solution. — Thirty grms. of pure iodide of potassium are dissolved in 100 c.c. of water in a flask of 1 litre capacity and furnished with a lateral tube. Through this solution, a current of well-washed chlorine is passed. As soon as the iodine is deposited in the form of a voluminous loose mass, the flask should be agitated for the purpose of dissolving this iodine. When the solution is complete, chlorine should be again passed through the now deep yellow liquid for another two minutes. After standing for five or six hours in a cool place, the solution deposits a crystalline mass formed of a combination of iodic acid and iodate of potassium. If the crystallisation is slow in appearing, it is only necessary to throw into the solution a few crystals of iodate of potassium to cause it to start. The crystals are separated by filtration, washed, and the filtrate, with the washings, are together diluted up to 1 litre. From this chloro-iodised solution we prepare a titrated solution, of which 10 c.c. added to 10 c.c. of a solution of iodide of potassium (20 grms. KI to 100 c.c. of water) corresponds exactly to 40 c.c. of a decinormal solution of hyposulphite of soda (27·8 grms. per litre). The hyposulphite solution is controlled by a decinormal solution of iodine.

The chloro-iodised solution thus prepared will keep for years without changing.

Preparation of the Solution of the Fatty Substance.— In the case of liquid fatty matters, exactly 10 c.c. are taken with a pipette, the temperature being brought to 15° C., and allowed to run slowly into a flask fitted with a ground-glass stopper; the pipette must not be blown into. Into the same flask 10 c.c. of chloroform are run from a burette. To rinse the pipette, it is filled with the solution of the fatty substance in chloroform, and allowed to run out slowly, at the same time stirring the contents of the flask with the pipette. By repeating this operation three times, we eventually get a homogeneous solution. If we have to deal with solid or semi-fluid bodies, such as butter, tallow, or castor oil, they must be first heated to 50°. If the value of iodine is not determined immediately, the flasks containing the mixtures must be kept in a cool place away from the light.

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Determination of the Titration Value of the Iodine.—I would first remark that I make no difference between siccative and non-siccative oils. For measuring the chloroform solution of the fatty body I use a 1 c.c. burette divided into hundredths of a c.c. After having filled the burette by aspiration, I run 0·4 c.c. of of the solution into a flask of 250 c.c. capacity fitted with a ground-glass stopper. After waiting five minutes for the liquid which adheres to the surface of the pipette to run into the flask, I add 10 c.c. of chloroform. The 20 c.c. of the chloro-iodised solution which it is now necessary to add to the contents of the flask cannot be measured exactly with a burette; but concordant results can be obtained with a 20 c.c. pipette, which must be subsequently rinsed with 4 c.c. of water, which are also added to the contents of the flask.

The flask must now be carefully shaken, but care must be taken that the stopper is not wetted, or there would be a liability to errors. The flask is then plunged half-way into water at about 10° (9° to 11°) and kept there for twenty-four hours away from the light. During the first six hours the flask must be shaken six times at regular intervals. At the end of the twenty-four hours the titration is done in the ordinary manner.

Example: Linseed Oil.—Twenty c.c. of the chloro-iodised solution require 80 c.c. of the hyposulphite solution (10 c.c. = 0·127 I). After the action of the fatty matter the 20 c.c. of the chloro-iodised solution required only 67·8 c.c. of hyposulphite: 80 − 67·8 = 12·2.

$$\frac{12{\cdot}2 \times 0{\cdot}127}{10} = 0{\cdot}1549.$$

$$\frac{0{\cdot}1549 \times 100}{0{\cdot}2} = 77{\cdot}4 = \text{value of iodine.}$$

In the following table I have given the iodine values as determined by my method on several fatty substances I had at my disposal.

Fatty Substances of Vegetable Origin.

	Iodine value. Aschmann.	Hübl.
Olive oil (Nice)	77·4	78·5 to 84
„ (Genoa)	74·9	—
Poppy-seed oil..	122 5	134 to 136
Oil of earth nuts	100·3	103
Sweet almond oil	95·0	98·4
Oil of sesamy	98 4	106
Linseed oil	142·8	148 to 158
Brown colza oil	92·7	100·4 to 1 2 8
White colza oil	92 7	—
Cotton-seed oil	104·7	1 6 to 110
Castor oil..	81·28	84·4
Cocoa-nut oil	5 08	8·9 to 9·4

Fatty Substances of Animal Origin.

Cod-liver oil (from the Indies)	1 6·0	—
„ white	133·3	—
„ brown	128 2	—
Tallow	52·0	57·1 to 6
Beef fat	35 5	40 to 44
Goat butter	24 1	—

Margarines.

	Iodine value (Aschmann).
1.	50·8
2.	63·5
3.	57·2
4.	55·2
5.	56·5
6.	58·4
7.	55·9

Butters.

1.	From the Milk Company	33·60	(26·0 to 35·1
2.	„ „	33·60	according to
3.	„ „	36·50	Hübl).
4.	„ „	35·50	
5.	„ „	37·90	
6.	„ „	34·90	
7.	„ „	34·90	
8.	„ „	36·20	
9.	„ „	34 90	
10.	„ „	35 50	
11.	„ „	36·20	
12.	Butter from the Market .	42 50	
13.	„ „	31·75	
14.	„ „	31·20	
15.	„ „	36·20	
16.	„ „	31·10	
17.	„ „	35·50	
18.	„ „	32·30	
19.	„ „	31·10	
20.	„ „	31·20	
21.	„ „	29 80	
22.	„ „	34·90	
23.	„ „	29 80	
24.	„ „	36 50	
25.	„ „	38·70	

—*Chemiker Zeitung*, p. 59, 1898.

UNIFORM METHODS FOR THE ANALYSIS OF FATTY BODIES.

By F. ULZER.

Index of Acidity.—By reason of the variations of the index of acidity according to the nature of the fatty body under examination, it is impossible to fix *à priori* the weight of the sample to work upon. This must be taken approximately in inverse ratio to the value of the index of acidity. As a rule we work on from 5 to 10 grms. The fat must be dissolved in ether, to which is added an equal volume of alcohol, and titrated with an aqueous or alcoholic solution of demi-normal soda (or deci-normal if the acidity is low), in the presence of phenolphthalein. If the acidity is very low 20 or 30 grms. of the sample may be taken, add 100 c.c. of perfectly neutral alcohol, shake carefully, and titrate with demi-normal soda.

Index of Saponification.—In preparing the alcoholic potash it is necessary to follow Henrique's instructions, and boil the powdered potash with alcohol at 95° in a flask fitted with a vertical condenser. If dilute alcohol is used the results will not be in concordance.

There are two methods of saponification:—

1. *Warm Saponification.*—2 to 2·5 grms. of the substance are treated with 25 c.c. of demi-normal potash and 25 c.c. of alcohol; boil for half an hour in a flask fitted with a vertical condenser, and titrate the excess of alkali with demi-normal hydrochloric acid. In the case of waxes it is necessary to add 10 c.c. of petroleum ether boiling at 100° C.

2. *Cold Saponification.*—There are two cases to consider:—

a. Neutral Fats.—We dissolve 3 or 4 grms. of the substance in 25 c.c. of cold petroleum ether, add 25 c.c. of a deci-normal solution of soda, shake well, and allow to stand for twelve hours at the ordinary temperature, and titrate as in the former case,

b. Waxes.—We use warm petroleum ether, and add soda lye immediately; heat to complete the solution, and allow to stand for twenty-four hours. Finally we titrate with demi-normal hydrochloric acid, taking care to heat the solution several times during the titration. The petroleum ether used should not boil below 100° C.

Index of Iodine.—As good results are obtained with Hübl's as with Waller's reagent. If we arrange that the

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excess of iodine be kept at double the amount of iodine absorbed, the time of the reaction will not exceed six hours. The solution of iodine, which should be prepared forty-eight hours before it is used, must be of such a strength that 25 c.c. of this solution will require at least 35 c.c. of decinormal hyposulphite for its saturation. For siccative oils and fish oils we use 0·1 to 0·2 grm., for non-siccative oils 0·2 to 0·25 grm., for suet fats 0·5 grm., and for palm oil or cocoa-nut oil about 1 grm. The substance is dissolved in 15 c.c. of pure chloroform, we add 25 c.c. of the iodine solution, and let stand for six hours. For titrating we use 25 c.c. of a 10 per cent solution of iodide of potassium. If there are a large number of determinations to make it is preferable, before commencing the back titration, to determine by a check experiment if the strength of the solution has varied, and to what degree. Account must be kept of this variation in calculating out the results. The conditions of the operation are exactly the same for Hübl's reagent as for Waller's.—*Chem. Rev. Fett. u. Harz. Ind.*, iv., [22], p. 299.

RESEARCH ON COMMERCIAL INCANDESCENT GAS MANTLES.

By E. HINTZ.

The author has already shown that the lighting power of mantles containing 99 per cent of oxide of thorium, and 1 per cent of oxide of cerium, was not influenced by the addition of 1 per cent of oxide of neodymium, lanthanum, or yttrium, or by the addition of 0·2 to 1 per cent of oxide of zirconium, while the effect of even 2 per cent of oxide of zirconium remained doubtful.

Following up his researches the author has obtained a large number of interesting results, which are here given in brief. In the following lines the normal mixture of 99 parts of oxide of thorium, and 1 part of oxide of cerium, will be called "thorium-cerium."

The following are the general conclusions arrived at:—

1. The addition of less than 0·2 per cent of oxide of zirconium to the thorium-cerium does not influence its lighting power. From this point of view then, oxide of zirconium can be classed with the other oxides.

2. When we add to the thorium-cerium a maximum of 2 per cent of neodymium, lanthana, or yttria, the lighting power is not affected, but it is slightly lowered by the addition of 2 per cent of oxide of zirconium.

3. In the presence of larger proportions of foreign oxides, the lighting power of the thorium-cerium mantles is nearly always diminished. A large proportion of neodymium or of yttria is more prejudicial than an equal quantity of zirconia or lanthana.

Table I. contains some characteristic results on this subject:—

TABLE I.

Composition of the mantles.	Maximum lighting power in Hefner units.	Consumption of gas in litres per hour. Total.	Per Hefner unit.
Thorium-cerium .. 95 / Zirconia 5	43	123	2·9
Thorium-cerium .. 80 / Zirconia 20	50	105	2·1
Thorium-cerium .. 95 / Neodymium 5	66	120	1·8
Thorium-cerium .. 80 / Neodymium 20	40	143	3·6
Thorium-cerium .. 95 / Lanthana 5	73	135	1·9
Thorium-cerium .. 80 / Lanthana 20	54	124	2·3
Thorium-cerium .. 95 / Yttria 5	62	126	2·0
Thorium-cerium .. 80 / Yttria 20	38	121	3·2

Effects Produced by Varying the Proportions of Thorium and Cerium.—To prepare oxide of thorium ThO_2 in a state of purity, the thorite was decomposed by hydrochloric acid, and the solution treated with sulphuretted hydrogen, and then with oxalic acid according to the now well-known method.

The precipitated oxalates were digested with oxalate of ammonia; the solution was considerably diluted, left to stand for some time, and filtered. The oxalates were re-precipitated by acidulating the filtered liquid with hydrochloric acid. Finally they were successively transformed into oxides, sulphates, hydrates, and chlorides; the slightly acid and dilute solution of the chlorides was precipitated by hyposulphite of soda; the precipitate was re-dissolved in hydrochloric acid, re-precipitated, and again dissolved in hydrochloric acid. The hydrate of thorium was finally precipitated with ammonia, and then transformed into nitrate. The solution contained 14·5 per cent of the oxide ThO_2.

A solution of pure oxide of cerium was also prepared, and it was into a suitable mixture of the two solutions that the tissue was plunged. The mantles were incinerated for from twenty-five to fifty minutes before being tested.

In Table II. are given the most interesting observations made by the author:—

TABLE II.

Composition of the mantles.	Lighting power in Hefner units.	Consumption of gas in litres per hour. Total.	Per Hefner unit.
Pure oxide of thorium ..	2·6	130	50
Pure oxide of cerium ..	2·0	125	61
Oxide of thorium .. 99·9 / „ cerium .. 0·1	17·0	115	6·7
„ thorium .. 99·8 / „ cerium .. 0·2	41·0	129	3·1
„ thorium .. 99·5 / „ cerium .. 0·5	62·0	133	2·1
„ thorium .. 99·0 / „ cerium .. 1·0	71·0	101	1·4
„ thorium .. 98·0 / „ cerium .. 2·0	61·0	101	1·7
„ thorium .. 97·0 / „ cerium .. 3·0	50·0	101	2·0
„ thorium .. 95·0 / „ cerium .. 5·0	40·0	101	2·4
„ thorium .. 90·0 / „ cerium .. 10·0	11·0	101	9·5
„ thorium .. 80·0 / „ cerium .. 20·0	8·4	101	12·0
„ thorium .. 60·0 / „ cerium .. 40·0	3·3	101	31·0
„ thorium .. 30·0 / „ cerium .. 70·0	2·2	103	48·0

With regard to the constancy of the lighting power the following facts were observed:—

A mantle containing 99·9 per cent of oxide of thorium, and 1 per cent of oxide of cerium, and giving 17 Hefner units at the first, with a consumption of gas of 115 litres per hour, gave, after 800 hours burning, 7·5 Hefner units, with a consumption of 114 litres of gas per hour. Another mantle containing 99·5 per cent of oxide of thorium, and 0·5 per cent of oxide of cerium, giving at first 40 Hefner units, with a consumption of 115 litres of gas per hour, gave, after burning 400 hours, a light of 27 Hefner units, with an hourly consumption of 116 litres of gas, and at the end of 800 hours its lighting power had fallen to 22 units for a consumption of 115 litres of gas per hour. Finally, a mantle containing 99 per cent of oxide of thorium, and 1 per cent of oxide of cerium, give, at these times, 54 units with 115 litres, 38 units with 116 litres, and 32 units with 114 litres.—*Zeitschrift für Analytische Chemie*, xxxvii. [8], p. 504.

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ON THE CAUSE OF THE RETENTION AND RELEASE OF GASES OCCLUDED BY THE OXIDES OF METALS.*

By THEODORE WILLIAM RICHARDS.

(Continued from p. 29).

It remains only, as far as zincic oxide is concerned, to show how wide a difference in the amount of gas may be caused by the original mode of preparation of the solid material.

The Effect of Physical Condition upon the Total Amount of Gas retained by Zincic Oxide.

	C.c. gas.
53. 1 grm. of ZnO, prepared from zincic carbonate at 880°, gave	0·00
54. 1 grm. of ZnO, prepared from zincic carbonate at 880°, gave	0·00
Average	0·00
55. 1 grm. of ZnO, prepared from the nitrate at 280°, not ignited, gave	0·01
56. A similar experiment gave	0·02
Average	0·015
57. 1 grm. of ZnO, prepared from zincic nitrate, but heated to 880° in a slightly reducing atmosphere, gave	0·05
58. A similar experiment gave	0·15
Average	0·10
42. 1 grm. of ZnO, prepared by gentle heating of the nitrate at 280°, and subsequent ignition for 30 minutes at 880° in an oxidising atmosphere, gave	0·192
43. A similar experiment gave	0·192
Average	0·192
59. 1 grm. of similar ZnO, prepared in the same way, but heated to 670° for 3 hours and then preserved two weeks before heating ½ hour at 880°, gave	0·292
60. A similar experiment gave	0·260
Average	0·276
61. 1 grm. of more compact ZnO, prepared by heating the nitrate rapidly, and having been preserved for two weeks before being ignited for ½ hour at 880°, gave	0·387
62. A similar experiment gave	0·396
Average	0·392

The evidence of these results proves that the total amount of gas retained by zincic oxide varies with every detail of the method of preparation; hence this amount cannot serve as a sure guide to the temperature of ignition, unless a perfectly uniform sample is used for all trials.† Of course the amounts of nitrogen found in these samples varied widely; for the gas resulted from the decomposition of zincic nitrate, which was imprisoned in varying quantities according to the physical condition of the zincic oxide.

Since so many circumstances regulate both the amount of gas and its composition, one is not surprised that Morse and Arbuckle obtained varying mixtures with eight different preparations of zincic oxide. It is true that their expulsion of the gases continued until it had become so slow that two successive weighings with intermediate heating gave constant weight; but the same causes of change must still have been at work, although far more slowly.

In the light of these interesting results, it seemed worth while to make a more elaborate investigation of the relation of the composition of the gases held by *cupric* oxide to the temperature used in its ignition. The material used in the following determinations was the soft powder made by the decomposition of cupric nitrate at 280°.

The Effect of Temperature of Ignition on the Composition of Gases retained by Cupric Oxide.

Time of Ignition, 1 hour.

	Per cent oxygen.
63. 0·32 c.c. gas from 1 gr. CuO heated at 520° contained	18
64. 0·34 „ „ „	15
Average	15·5
65. 0·49 c.c. gas from 1 gr. CuO, heated at 660° contained	6
66. 0·48 „ „ „	5
Average	5·5
67. 0·47 c.c. gas from 1 gr. CuO, heated at 750° contained	3
„ „ „ „	4
Average	3·5

0·05 c.c. gas from 1 gr. CuO, heated at 1000°± contained 0 to 4 per cent oxygen, according to Alexander Scott.

It is evident that the cupric nitrate remaining in the cupric oxide had not been wholly decomposed by heating for an hour at 500° (experiments Nos. 63 and 64), and that we are dealing here with an increasing total, and a maximum similar in every respect to that already noted in the case of zinc, except that in the present case more nitrogen is held, while the oxygen escapes at a much lower temperature.

The Effect of Time on the Composition of the Gas retained by Cupric Oxide.

First Series: Temperature, 500°.
(Argentic Chloride easily melted; Plumbic Chloride scarcely melted).

	Per cent oxygen.
68. 0·29 c.c. gas from 1 gr. CuO, heated 2 hours contained	25
69. 0·29 „ „ „	23
Average	24
70. 0·38 c.c. gas from 1 gr. CuO, heated 8 hours contained	15
71. 0·42 „ „ „	14
Average	14·5
72. 0·46 c.c. gas from 1 gr. CuO, heated 16 hours contained	8

Second Series: Temperature, 520°.
(Just below the melting-point of Argentic Iodide, but distinctly above that employed in the last series).

73. 0·15 c.c. gas from 1 gr. CuO, heated for 15 min., contained	23
63. 0·32 c.c. gas from 1 gr. CuO, heated for 1 hr., contained	18
64. 0·34 „ „ „	15
Average	16·5

* Contributions from the Chemical Laboratory of Harvard College. From the *Proceedings of the American Academy of Arts and Sciences*, xxxiii., No. 23; also *American Chemical Journal*, November, 1898.

† Small quantities of such impurities as alkali and silica do not seem to affect the occlusion, however. See *Proc. Amer. Acad.*, xxviii., 207.

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	Per cent oxygen.
74. 0·48 c.c. gas from 1 gr. CuO, heated for 2 hrs., contained	12
75. 0·40 c.c. gas from 1 gr. CuO, heated for 16 hrs., contained	6

Third Series: Temperature, 600°.
(Argentic Iodide fused easily; Lithic Chloride fused slowly).

76. 0·43 c.c. gas from 1 gr. CuO heated for 10 min., contained	12
77. 0·38 „ „ „	12
Average	12
78. 0·46 c.c. gas from 1 gr. CuO, heated for 20 min., contained	13
79. 0·53 c.c. gas from 1 gr. CuO, heated for 35 min., contained	10
80. 0·51 „ „ „	8
Average	9

Fourth Series: Temperature, 640°.
(Thallous Sulphate just fused; Strontic Nitrate remained solid).

81. 0·21 c.c. gas from 1 gr. CuO, heated for 2 mins., contained	35
82. 0·19 „ „ „	36
Average	35·5
83. 0·43 c.c. gas from. 1 gr. CuO, heated for 10 min., contained	19
84. 0·45 „ „ „	16
Average	17·5
85. 0·46 c.c. gas from 1 gr. of CuO, heated for 8 hrs., contained	6
86. 0·45 „ „ „	4
Average	5

It is clear that we are dealing here with a phenomenon precisely similar to that observed in the case of zinc. The decomposition of the remaining traces of nitric anhydride takes place much more slowly at low temperatures than at high ones, and the oxygen formed by this decomposition is liberated far more rapidly during the hotter ignitions.

A single series of experiments (*Proc. Amer. Acad.*). xxviii., 209), made some years ago with magnesic oxide), shows that this substance too acted in the same way, and it is probable that all the other oxides retaining traces of occluded gases would give similar results. The data obtained from magnesic oxide are repeated below, in order that all the facts may be at hand for the following consideration of the causes of the anomaly.

Gas Evolved from Magnesic Oxide.

(Temperature of Ignition was about 700°—800°.

1 grm. MgO after ignition 30 minutes gave 3·60 c.c. nitrogen and 7·2 c.c oxygen.
1 grm. MgO after ignition 60 minutes gave 4·72 c.c. nitrogen and 6 3 c.c. oxygen.
1 grm. MgO after ignition 75 minutes gave 4·84 c.c. nitrogen and 4·4 c.c. oxygen.
1 grm. MgO after ignition 135 minutes gave 5·44 c.c. nitrogen and 3·6 c.c. oxygen.
1 grm. MgO after ignition 195 minutes gave 5·24 c.c. nitrogen and 2·8 c.c. oxygen.

(To be continued).

DERIVATIVES OF THE TETRACHLORIDES OF ZIRCONIUM, THORIUM, AND LEAD.*

By J. MERRITT MATTHEWS.

(Concluded from p. 33).

H. *Quinoline.*

a. Zirconium Tetrachloride, $ZrCl_4 \cdot 2C_9H_7N$.—0·6140 grm material gave:—

0·6977 grm. silver chloride = 0·1727 grm. chlorine = 28·12 per cent chlorine.
0·1592 grm. zirconium dioxide = 0·1177 grm. zirconium = 19·17 per cent zirconium.

0·7226 grm. material gave:—
0·0478 grm. ammonia = 0·0394 grm. nitrogen = 5·45 per cent nitrogen.

	Calculated for $ZrCl_4 \cdot 2C_9H_7N$.	Found.
Chlorine	28·94	28·12
Zirconium	18·47	19·17
Nitrogen	5·72	5·45

b. Thorium Tetrachloride, $ThCl_4 \cdot C_9H_7N$.—0·4110 grm. material gave:—

0·4634 grm. silver chloride = 0·1147 grm. chlorine = 27·91 per cent chlorine.
0·2175 grm. thorium dioxide = 0·1911 grm. thorium = 46·50 per cent thorium.

0·4212 grm. material gave:—
0·0129 grm. ammonia = 0·0106 grm. nitrogen = 2·52 per cent nitrogen.

	Calculated for $ThCl_4 \cdot C_9H_7N$.	Found.
Chlorine	28·19	27·91
Thorium	46·18	46·50
Nitrogen	2·78	2·52

c. Lead Tetrachloride, $PbCl_4 \cdot 2C_9H_7N$.—Quinoline reacted very energetically with lead tetrachloride, yielding a lemon-yellow precipitate which proved to be quite stable.

0·3012 grm. material gave:—
0·2806 grm. silver chloride = 0·0695 grm. chlorine = 23·06 per cent chlorine.

0·2298 grm. material gave:—
0·1140 grm. lead sulphate = 0·0779 grm. lead = 33·90 per cent lead.

0·2792 grm. material gave:—
0·0845 grm. platinum = 0·0121 grm. nitrogen = 4·34 per cent nitrogen.

	Calculated for $PbCl_4 \cdot 2C_9H_7N$.	Found.
Chlorine	23·39	23·06
Lead	34·10	33·90
Nitrogen	4·61	4·34

I. *β-Naphthylamine.*

a. Zirconium Tetrachloride, $ZrCl_4 \cdot 2C_{10}H_7NH_2$.—On adding a solution of naphthylamine in anhydrous ether to a solution of zirconium tetrachloride a greyish brown precipitate was produced, the analysis of which approximated to the formula given above.

0·5736 grm. material gave:—
0·6419 grm. silver chloride = 0·1589 grm. chlorine = 27·70 per cent chlorine.
0·1397 grm. zirconium dioxide = 0·1032 grm. zirconium = 18·00 per cent zirconium.

0·7012 grm. material gave:—
0·0426 grm. ammonia = 0·0351 grm. nitrogen = 5·01 per cent nitrogen.

* Contribution from the John Harrison Laboratory of Chemistry. From the *Journal of the American Chemical Society*, xx., No. 11. From author's thesis for the Degree of Doctor of Philosophy.

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	Calculated for $ZrCl_4 \cdot 2C_{10}H_7NH_2$.	Found.
Chlorine	27·38	27·70
Zirconium	17·47	18·00
Nitrogen	5·41	5·01

b. Thorium Tetrachloride, $ThCl_4 \cdot C_{10}H_7NH_2$. — This derivative was greyish white in colour and comparatively stable in the air.

0·2582 grm. material gave :—
0·2844 grm. silver chloride = 0·0704 grm. chlorine = 27·27 per cent chlorine.
0·1329 grm. thorium dioxide = 0·1168 grm. thorium = 45·25 per cent thorium.

0·6045 grm. material gave :—
0·0166 grm. ammonia = 0·0137 grm. nitrogen = 2·27 per cent nitrogen.

	Calculated for $ThCl_4 \cdot C_{10}H_7NH_2$.	Found.
Chlorine	27·43	27·27
Thorium	44·94	44·25
Nitrogen	2·70	2·27

c. Lead Tetrachloride, $PbCl_4 \cdot C_{10}H_7NH_2$.—Naphthylamine gave a dark green precipitate with lead tetrachloride in a dilute solution; in more concentrated solutions the naphthylamine was apparently decomposed.

0·2276 grm. material gave :—
0·2604 grm. silver chloride = 0·0645 grm. chlorine = 28·32 per cent chlorine.

0·3006 grm. material gave :—
0·1914 grm. lead sulphate = 0·1307 grm. lead = 43·47 per cent lead.

0·2416 grm. material gave :—
0·0544 grm. platinum = 0·0079 grm. nitrogen = 3·24 per cent nitrogen.

	Calculated for $PbCl_4 \cdot C_{10}H_7NH_2$.	Found.
Chlorine	28·86	28·32
Lead	42·07	43·47
Nitrogen	2·84	3·24

J. *Acid Amides.*

The action of acetamide and benzamide was tried on the solutions of the tetrachlorides, but no compound resulted in any case, the acid amides evidently not being sufficiently basic to form derivatives like the amines.

Diphenylamine was also tried, but it gave no reaction with either the zirconium or thorium salt. The lead salt gave a deep blue solution and lead chloride separated out, showing that the lead tetrachloride in this case acted like bleaching lime on diphenylamine.

5. General Remarks.

On comparing the derivatives of the three tetrachlorides here used, many similarities will at once be evident. In order to facilitate with such a comparison it will not be superfluous to present a tabular *résumé* of the various derivatives herein prepared and described.

	With $ZrCl_4$. Mols. amine.	With $ThCl_4$. Mols. amine.	With $PbCl_4$. Mols. amine.
Ammonia (from solution)	8	8	4, 2
Ammonia (without heat).	2	6	
Ammonia (with heat) ..	4	6	
Methylamine	4	4	4
Ethylamine	4	4	4
Propylamine	4	4	4
Aniline	4	4	3
Toluidine	4	3	Decomp.
Pyridine	2	1	2
Quinoline	2	1	2
Naphthylamine	2	1	1
Diphenylamine ..	No reaction.	No reaction.	Decomp.
Acid amides			No reaction.

Nearly all these derivatives are stable in the air, the only noticeable exceptions being the pyridine, quinoline, and the lower ammonia compounds of zirconium and thorium. None of them show any tendency toward a crystalline structure, but come down as amorphous precipitates resembling hydroxides.

On heating these compounds in the air they readily split up into the amine hydrochloride and the dioxides; with lead, however, lead dichloride is left on ignition. They are also decomposed when treated with water, and the fixed alkalis precipitate the hydroxides of the three metals.

It will also be noticed that the majority of these derivatives seem to obey the law of Remsen in its application to molecular compounds; and the tendency is apparently toward an even number of molecules, though several of the thorium and lead derivatives deviate from this general law in having an odd number of additive molecules.

Two of the chlorine atoms in lead tetrachloride are very loosely combined, splitting off at the slightest disturbance to the chemical equilibrium of the compound; and yet it is of interest to note that the amines seem to fix these two atoms of chlorine into a more stable form, doubtless due to some peculiar internal linking in the compound. That these two atoms of chlorine are exceedingly active is seen by the behaviour of lead tetrachloride with toluidine, where no additive compound could be obtained, as the amine was decomposed even with dilute solutions, giving rise no doubt to complex chlorinated and condensed products. In fact, concentrated solutions of lead tetrachloride will decompose any of the aromatic amines, with the production of blue, purple, and green coloured solutions and resinous products. In this great activity of two of its atoms of chlorine, lead tetrachloride differs widely from the corresponding salts of zirconium and thorium, as these latter show no tendency to break down to lower chlorides.

THE OCCURRENCE OF COPPER IN THE PLANT WORLD.

By G. B. FRANKFORTER.

It has frequently been stated that the metal copper occurs in both plants and animals. Neubauer (*Zeit. Anal. Chem.*, v., 260) found, on careful examination, that animal tissue invariably contained a very small quantity of copper. He found, on analysing the tissue of various carnivorous animals, that 1 grm. of ash from the tissue contained from one- to two-tenths of a m.grm of copper. Bergeron and l'Hôte (*Comptes Rendus*, lxxx., 268) confirmed the above statement, giving special attention to the organs of the Mammalia. They invariably found copper in the liver and kidneys in comparatively constant quantities.

Ulex (*Journ. Prakt. Chem.*, xcv., 367; xcvi., 460) made an exhaustive examination of the tissue of various animals, and found copper in every instance. His experiments, however, were repeated by Lossen, who reached entirely different conclusions. Lossen showed that the copper found by Ulex came entirely from the Bunsen burner and other utensils containing copper with which he performed his experiments. So careful were his analyses that it seems impossible to doubt his conclusion. It seems possible, therefore, that the copper found by Neubauer and others may have come from similar sources. At any rate, it remains for future experiments to determine the exact extent of copper in the animal world.

Several announcements have been made of the occurrence of copper in the plant world. The general conclusion has been that plants growing on soil which contains copper, assimilate small quantities. Dieulafait (*Ann. Chim. et de Phys.* [5], xviii., 349), in an exhaustive treatise

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on the distribution of copper in the primordial rocks, found copper widely distributed, ranging in quantity from a mere trace to great beds of the metal. He likewise showed that certain of the carbonate rocks contained appreciable quantities of the metal. The dolomites were invariably found to contain copper, while the lime carbonates were nearly always free from the metal. In a second paper (*Ann. Chim. et de Phys.* [5], xix. 550) Dieulafait showed that plants growing on a dolomitic soil, as well as a soil from the primordial rocks, contained an appreciable quantity of copper, while those growing on a limestone soil rarely ever contained a trace of copper.

There can be little doubt, at the present time, concerning Dieulafait's conclusion as to the distribution of copper in the various rocks. His conclusion as to its distribution in plants, however, remains somewhat uncertain, and much must be done before his conclusion may be fully and logically reached.

An interesting instance of the occurrence of copper in the plant world, however, came under my observation recently. While removing an oak tree which grew within the limits of the city of Minneapolis, and which had recently died, a gentleman noticed, in cutting up the trunk, a considerable quantity of bright copper-coloured powder disseminated through the pores of the wood. A quantity of this powder was examined, and found to be pure metallic copper. This strange coincidence led to a series of analyses of the different parts of the tree. A careful preliminary examination, preparatory to the analysis, showed certain parts of the tree to be thoroughly impregnated with this granular copper powder. Some of these granules were so large as to take on the form of flakes. The larger ones were partly rolled up so as to fit in the irregular pores of the wood. When unrolled, the large flakes measured 1½ m.m. in diameter.

The powder was then analysed, giving the following results:—

0·0608 grm. of the powder gave 0·0578 grm. of copper.
Per cent of copper 95·01.

In the microscopic examination of the powder a very small quantity of a white crystalline substance was observed, but the quantity was too small for an examination. Could these fine crystals have been removed, the copper would undoubtedly have been found unusually pure.

An Examination of the Wood.

In order to determine how thoroughly the copper was disseminated throughout the whole tree, a microscopical examination and several analyses were made. The microscopical examination revealed the fact that only the outer annual rings contained an appreciable quantity of the metal. The last six or seven annual rings were so full of these flakes of copper that they could easily be discerned by the naked eye. The earlier rings showed only a trace under the microscope and by analysis, and those nearest the heart were quite free from the metal.

The first conclusion was that, the soil here being dolomitic, the tree had assimilated copper from that source. The above facts plainly show that such cannot be the case, else the copper would be evenly distributed throughout the different parts of the tree. The following analyses serve to show how unevenly the metal was distributed through the wood:—

Analysis No. 1.—Wood taken from the heart of the tree: 500 grms. of wood gave 4·6 grms. of ash and 0·004 grm. of copper.

Analysis No. 2.—Wood taken from the tree about halfway between the heart and bark: 300 grms. gave 3·765 grms. of ash and 0·0056 grm. of copper.

Analysis No. 3.—Wood taken from near the bark: 200 grms. gave 2·86 grms. of ash and 0·0079 grm. of copper.

Analysis No. 4.—Wood taken representing an average of the whole tree: 350 grms. of wood gave 3·84 grms. of ash and 0·0042 grm. of copper.

Analysis.	Per cent of ash.	M.grms. of copper per 100 grms. of wood.
No. 1.	0·92	0·8
No. 2.	1·28	1·86
No. 3.	1·43	3·95
No. 4.	1·1	1·2

In these analyses every precaution was taken to eliminate any possibility of error from apparatus used. It would seem, from the uneven distribution of the copper, that the tree was not accustomed to such quantities of the metal, and that it had absorbed the metal within the last few years, a probable cause of its death.

The origin of the copper has not yet been determined. Native copper occurs here in the soil, and that at present would seem to be the most reasonable explanation of its source. If such is the case, then the plants of the Lake Superior Region, where native copper is still more abundant, should contain considerable quantities of copper. Experiments will be conducted along this line, in order to determine whether or not this occurrence is common there.

The fact that copper was found here in the metallic state raises the question of the form in which it exists in plants in general. Although nothing has been done along this line, it is reasonable to suppose that the metal is taken up in the form of some soluble salt. The genera form in which it left in plants must be determined by future experiments,

The University of Minnesota,
Minneapolis.

CERTAIN ALKALOIDAL PERIODIDES, AND THE VOLUMETRIC ESTIMATION OF ALKALOIDS AS HIGHER PERIODIDES.*

By A. S. PRESCOTT and H. M. GORDIN.

(Continued from p. 31).

Verification of the Equation for the Iodine Factor.

Partly from the fact that Kippenberger (*Ztschr. Anal. Chem.*, xxxv., 10; xxxiv., 317: on this question also see Gomberg, 1896; *Journ. Am. Chem. Soc.*, xviii., 332) has proposed a different reaction in the formation of periodide precipitates, and for other reasons, we thought it advisable to prove irrefutably that the iodide of potassium of the iodine solution takes an active part in the reaction by which the atropine enneaiodide, as an example, is formed and gives off an amount of iodine which is just equal to the amount of the normal iodine of the enneaiodide.

We proceeded in the following manner:—We first determined the strength of our iodine solution with regard to free iodine; this was done by means of a sodium thiosulphate solution of known strength. We then took 10 c.c. of this iodine solution and determined the total amount of iodine, free as well as bound to potassium, by shaking them in a flask with an excess of powdered metallic zinc till the colour of iodine disappeared, filtering the solution of zinc iodide and potassium iodide thus obtained, washing the flask and the excess of zinc with hot water, and precipitating the iodides in the filtrate with silver nitrate and nitric acid. From the weight of silver iodide washed and dried in the usual way, we calculated the amount of total iodine present in our iodine solution. By subtracting the amount of free iodine from that of the total iodine, we obtained the amount of iodine present in our solution as potassium iodide. We thus found that the iodine solution contained 1 per cent free iodine and 1·2312 per cent combined iodine.

We then put 40 c.c. of this iodine solution in a 100 c.c. measuring flask, added 20 c.c. of a 3/10ths per cent solution of atropine alkaloid, and, after shaking well, diluted

* *Journal of the American Chemical Society*, xx., No. 9, Sept., 1898.

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the liquid in the flask to 100 c.c. We now took two phials, and in each filtered off 25 c.c. from the flask. In the first phial, the amount of free iodine titrated back with sodium thiosulphate was found to be 0·0465. From this it is easy to deduce that the 20 c.c. of the 3/10ths per cent atropine solution consumed 0·214 grm. of the free iodine. In the second phial the total iodine was determined in the same way as described above, and the quantity of silver iodide was found to be 0·3023 grm., which shows that after the treatment with atropine the liquid contained 1·633 per cent total iodine. From these data we deduce that the 20 c.c of the atropine solution have taken up 0·02528 grm. iodine from the bound iodine. As the 20 c.c. of atropine solution contained 0·06 grm. atropine, we find for 100 parts of precipitated enneaiodide:—

	Found. Per cent.	Calculated. Per cent.
Atropine..	20·05	20·26
Iodine taken from the free iodine of the iodine solution	71·50	70·88
Iodine from the iodine bound as KI	8·45	8·86

We see that in aqueous acidulous solutions the potassium iodide takes an active part in the reaction by joining in a yield of hydriodic acid for the normal hydriodide of the alkaloid, necessary to hold the additive iodine of the periodide. When carbon disulphide or carbon tetrachloride is used as a solvent for the atropine and the iodine, no periodide seems to be formed, possibly for the reason of there being no generation of hydriodic acid for the making of hydriodide. As to the formation of the periodides in chloroformic solution of atropine and iodine, it might possibly be explained by the substituting action of iodine either upon the chloroform or upon a side-chain of the atropine.

The direct substitution of iodine for some of the hydrogen in these bodies might, in this case, be made possible by the presence of the natural base, which combines with the hydriodic acid when formed by such a substitution. Part of the atropine would then act in a manner similar to that of mercuric oxide, which is usually employed in the iodising of hydrocarbons. An analogous case we have in the easy substitution of iodine for some of the hydrogen in aniline, a part of which combines with the hydriodic acid which is set free through the substitution of iodine for hydrogen in another part. At any rate we shall endeavour to determine the by-products formed when atropine enneaiodide is produced in chloroformic solutions.

Procedure in the Volumetric Method.

The general mode of procedure in the estimation of the strength of an aqueous solution of an alkaloidal salt is as follows:—To about 10 c.c. of decinormal iodine solution diluted with a little water, 1 c.c. of the acidulated alkaloidal solution is added, and the mixture well shaken for a few minutes. Should the precipitate separate out very quickly, and the clear supernatant liquid have only a light yellow or greenish colour, or be altogether colourless, the alkaloidal solution is too strong and must be diluted, till after a few trials the clear supernatant liquid retains a very dark red colour after the separation of the precipitate. The acidulated alkaloidal solution is then made up to a given volume, and 10 or 15 c.c. of it are run from a burette into a graduated vessel, into which has been previously put 25 or 30 c.c. decinormal iodine solution diluted with a little water. The mixture is then made up to a given volume and shaken till the supernatant liquid is perfectly transparent, and is of a very dark red iodine colour. This point is very important, and should the clear liquid not have this dark red colour the experiment with most alkaloids (except morphine and possibly some others, should be repeated, putting more decinormal iodine into the graduated vessel, or decreasing the number of c.c. of the alkaloidal solution. It would not do to add more decinormal iodine to the same mixture, as the iodine must be in large excess during the whole operation, in order to prevent the formation of lower periodides, which, once formed, might not take up fresh iodine and form higher periodides. Only with morphine, which in such solutions forms but one periodide, these precautions are unnecessary. When the liquid has become perfectly clear an aliquot portion of it is filtered off, and the excess of iodine determined by standard sodium thiosulphate. From these data are obtained the quantity of iodine consumed. This quantity of iodine, mulitiplied by the "ratio of alkaloid to 1 of iodine" gives the quantity of alkaloid sought. If preferred, but generally with less convenience to the chemist, the number of c.c. of decinormal solution of iodine consumed may be multiplied by the "alkaloidal factor of 1 c.c. N/10 I sol."

Verification of the Iodine Factors by Volumetric Control.

For Atropine.—In the following estimations of the strength of atropine solutions both the iodine solution and the sodium thiosulphate solution were strictly decinormal. Of the iodine solution 20 or 25 c.c. were put into a 100 c.c. measuring flask, and atropine solutions of known strength run in from a burette, and the operation continued as described above. When the supernatant liquid was perfectly transparent the flask was filled up to 100 c.c., and 50 c.c. were filtered off. In these 50 c.c. the excess was determined by means of the tenth normal thiosulphate solution, and the strength of the atropine solutions calculated by using the factor 0·0036048 for every c.c. of decinormal iodine used up.

	Actual strength. Per cent.	Number of c.c. of the atropine solution taken.	Number of c.c. of the tenth normal iodine used up.	Results in strength. Per cent.
1.	0·50	12	15·6	0·47
2.	0·40	15	14·9	0·36
3.	0·30	17	13·2	0·28
4.	0·25	12	10·0	0·28

For Strychnine.—To test the correctness of the ratio of 1 of free iodine to 0·4390 of strychnine, two solutions were prepared, one of 1 per cent, the other of 0·612 per cent of the alkaloid. The estimations, by the volumetric method, gave results as follows:—

	Actual strength. Per cent.	Strychnine solution taken. C.c.	Iodine consumed.	Results obtained. Per cent.
1.	1·0	3	0·07	1·026
2.	0·612	7	0·191	0·633

For Brucine.—Two solutions of the alkaloid were made, and estimated volumetrically, calculating by the ratio 1 part of iodine to 0·5179 part of anhydrous brucine, with these results:—

	Actual strength. Per cent.	Brucine solution taken. C.c.	Iodine consumed.	Results obtained. Per cent.
1.	1·0	10	0·193	0·999
2.	0·5	10	0·096	0·497

For Morphine.—Three standard solutions were made of strengths in anhydrous alkaloid as below tabulated. This was done by weighing a good article of well-crystallised morphine, free alkaloid, as $C_{17}H_{19}NO_3.H_2O$. The results were calculated by the ratio 1 of iodine to 0·74918 of morphine, absolute.

	Strength in per cent.	Morphine solution. C.c.	Iodine solution. C.c.	Iodine consumed.	Result in per cent.
1.	0·518	10	20	0·070116	0·525
2.	0·259	10	20	0·334272	0·257
3.	0·100	10	20	0·014023	0·105

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The Iodine Factors of the Alkaloids so far Determined.

Higher periodide formed.	Ratio of alkaloid to one of iodine.	Alkaloid factor of 1 c.c. tenth-normal iodide solution.
Atropine, $C_{17}H_{23}NO_3.HI.I_8$ ..	0·2849	0·0036048
Strychnine, $C_{21}H_{22}N_2O_2.HI.I_6$	0·4390	0·00555467
Brucine, $C_{23}H_{26}N_2O_4.HI.I_6$ ..	0·5179	0·00655299
Morphine, $C_{17}H_{19}NO_3.HI.I_3$..	0·74918	0·00947937
Aconitine, $C_{33}H_{45}NO_{12}.HI.I_6$.	—	—
By Gomberg in 1896 (*Journ. Am. Chem. Soc.*, xviii., 339):		
Caffeine, $C_8H_{10}N_4O_2.HI.I_4$ ..	0·3834	0·00485

(To be continued).

CORRESPONDENCE.

THE ESTIMATION OF MANGANESE BY MEANS OF POTASSIUM PERMANGANATE.

To the Editor of the Chemical News.

SIR,—I gather from Mr. F. W. Daw's article of last week that he considers the presence of carbon in the iron with which permanganate solutions are standardised to be an insufficient explanation of the low results obtained on using the permanganate to titrate manganous salts. At the same time I understand that Mr. Daw allows this to be a source of error when permanganate or even bichromate solutions are standardising by straightway titrating a solution of iron wire in dilute sulphuric or hydrochloric acid.

If the purity of the ferrous ammonium sulphate used, and particularly its freedom from carbonaceous matter, has been placed beyond doubt, then, of course, there must be some other reason for the low results.

Mr. Daw, I presume, is aware that the reaction between permanganate and manganous salts forms true MnO_2 as expressed by the equation only under certain conditions. The fact that he made no mention of such a possible source of error suggests that he thinks some other explanation is necessary. May I let the importance of the subject be my apology for troubling him to say whether he is able to explain the apparent anomaly?

I notice that in analysing the standard ferro-manganese the Mn_3O_4 precipitate is heated in a platinum crucible over a blast lamp. As platinum at high temperatures is permeable to gases, and as some of the gases of the flame may exert a reducing action, is not this procedure questionable in so delicate a matter?—I am, &c.,

HARRY BREARLEY.

Totley, near Sheffield.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

NOTE.—All degrees of temperature are Centigrade unless otherwise expressed.

Comptes Rendus Hebdomadaires des Séances, de l'Académie des Sciences. Vol. cxxvii., No. 23, December 5, 1898.

Action of Acetylene on the Ammonium Compounds of the Alkalis.—Henri Moissan.—The author has obtained the following acetylene acetylides by acting on the ammonium compounds of the alkaline metals with acetylene: — $C_2K_2.C_2H_2$, $C_2Na_2.C_2H_2$, $C_2Li_2C_2H_2.2NH_3$, $C_2Ca.C_2H_2.4NH_3$. All these compounds dissociate and leave the carbides or the corresponding acetylides, C_2K_2, C_2Na_2, C_2Li_2, C_2Ca. When the ammonia compounds are acted on by acetylene, hydrogenation of the acetylene takes place, and ethylene is produced. The acetylene compounds of the carbides are soluble in ammonia, and this property causes different reactions to take place at a low temperature.

Colour of Calcium Carbide.—Henri Moissan.—The author has conducted a series of experiments to discover whether the reddish brown appearance of the crystals of calcium carbide is due to an impurity or is a property of the salt itself. He finds that when the carbide is absolutely pure, it is quite transparent and colourless, but the merest trace of iron gives it the reddish brown appearance.

The Properties of Aluminium.—A. Ditte.—For some time aluminium has been considered to be a metal which resisted the greater number of chemical reagents. The author's experiments show that this is not the case. When the metal is placed in dilute acid it dissolves rapidly at first, but a layer of gas is deposited on the surface which resists further action. This layer is found to adhere very firmly to the metal. By getting rid of the gas as fast as it is formed, either by working at reduced pressure or by some other means, it is found that the metal dissolves away entirely. In the case of a solution of common salt, the following reaction takes place:— $Al_2+6NaCl+3H_2O=Al_2Cl_3+3Na_2O+3H_2+157{\cdot}3$ cals.; but a double decomposition follows,—

$$Al_2Cl_6+3Na_2O=Al_2O_3+6NaCl+287 \text{ cals.},$$

and the deposit of the layer of Al_2O_3 arrests further action. The same reaction occurs when a plate of aluminium is placed in a solution of a salt of the alkaline earths. In fact, the author's experiments tend to show that aluminium is attacked in a more or less marked manner by all chemical agents.

Displacement of Metals by Hydrogen.—Albert Colson.—The results which have been proved concerning the action of bases or of free acids on dry salts apply to the reciprocal displacements of the metals. For example, hydrogen, considered as a volatile metal, displaces silver and copper from their dry salts. This reaction should be reversible, since the substitution of the metals by hydrogen is endothermic; but it is not so, owing to the fact that the absorption of hydrogen increases with the temperature. The author has experimented on the displacement of silver by hydrogen in various salts under varying physical conditions.

Synthesis of Phenol by Acetylene.—M. Berthelot.—The author has effected many syntheses by means of acetylene, one of the most interesting being that of phenol, which is obtained either through the condensation of acetylene in benzine, or by the action of potash on a sulphonated derivative of acetylene. In both cases the synthesis only requires a temperature of about 200°.

No. 24, December 12, 1898.

The Mixed Phosphates of Ethyl and Phenyl.—Albert Morel.—The author has investigated the action of the di- or monochlor-alcoholic phosphates on phenols or phenolates of the alkalis, and has found that they produced mixed phosphoric ethers, identical with those formed by the action of triphenyl phosphate on alcoholates of the alkalis. The ethers selected were—

$PO\begin{cases}OC_6H_5\\OC_6H_6\\OC_2H_5\end{cases}$ and $PO\begin{cases}OC_6H_5\\OC_2H_5\\OC_2H_5\end{cases}$.

Details of their preparation and properties are given.

Transformation of the Carbonate of Orthocresol into a Homologue of the Phthalein of Orthocresol.—P. Cazeneuve.—The carbonate of orthocresol mixed with excess of soda-lime undergoes an interesting molecular transformation, resembling that of phenyl carbonate and sodium into sodium salicylate. The author gives the method of preparation of the new compound expressed by the following equations:—

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(i.) $2CO<^{OC_6H_4CH_3}_{OC_6H_4CH_3} + 2NaOH + O =$

$= CO.OH>CH_2 C_6H_3.CH<^{C_6H_3<^{OH}_{CH_3}}_{C_6H_3<^{OH}_{CH_3}} +$

$+ Na_2CO_3 + H_2O + C_6H_5OH;$

(ii.) $CO.OH>CH_2 C_6H_3.CH<^{C_6H_3<^{OH}_{CH_3}}_{C_6H_3<^{OH}_{CH_3}} + O =$

$= C<^{C_6H_3<^{OH}_{CH_3}}_{C_6H_3<^{OH}_{CH_3}}_{C_6H_3<^{CH_3}_{O\text{---}CO}} + H_2O.$

This molecular transformation is not observable in the cases of the carbonates of meta- and para-cresol.

Chlorination of Benzene in presence of Aluminium Chloride.—A. Mouneyrat and Ch. Pouret.—In a previous paper the powerful chlorinating action of $AlCl_3$, in the case of the members of the fatty series, was demonstrated. In the present article the application of the same reaction to hydrocarbons of the aromatic series is discussed. The results are similar in both cases. The aluminium chloride forms a chlorine carrier as efficient as iodine, and has the advantage of producing no by-products. The typical reaction is expressed as follows:—

1. $C_6H_6 + AlCl_3 = C_6H_5 - AlCl_2 + HCl.$
2. $C_6H_5 - AlCl_2 + Cl_2 = C_6H_5Cl + AlCl_3.$

Action of Oxidising Agents on certain Nitrogen Compounds.—Œchsner de Coninck.—The oxidising agents employed were chromic acid and potassium bichromate; and the oxidation of substances such as hydroxylamine, phenylhydrazine, guanidine, hydrazine, methane, acetamide, benzamide, urea, and ammonia compounds, was examined.

MISCELLANEOUS.

Institute of Chemistry.—January Examinations, 1899.—*Names of Candidates who Passed the Practical Examination for the Associateship:* Arthur Jenner Chapman, Ferdinand Edward Paul Forster, George Percy Lishman, B.Sc. (Edin.). *Intermediate Examination:* Stafford Aston, Walter Lionel Blackman, Basil Radcliffe Coyah, Henry Dixon Hewitt, Alfred Hill, Henry Wulff Kinnersley, John Rogers, Frank Shedden, B.Sc. (Lond.), Leonard Victor Wright, B.A. (Cantab.). *Final Examination for the Associateship.*—In Branch "A" (Mineral Chemistry): *John Golding, *Walter Charles Hancock, B.A. (Cantab.), Arthur Marshall, A.C.G.I. In Branch "B" (Metallurgical Chemistry): John Imrie, Roland Cecil Wild. In Branch "D" (Organic Chemistry: William Setten Gilles, A.C.G.I., Percy John Hinks, A.R.C.Sc. (Lond.), Thomas Goode Joyce, B.Sc. (Lond.). In Branch "E" (The Analysis of Food and Drugs, and of Water): *John Francis Hutchins Gilbard, Charles Adolphus Hackman, Francis Samuel Young, M.A. (Oxon). (Those marked with an asterisk for the Fellowship).

The Separation of Mercury and Bismuth.—MM. Vanino and Treubert.—This method of separation is based on the complete precipitation of the mercuric chloride in the state of mercurous chloride, in dilute hydrochloric solution, by a mixture of peroxide of hydrogen and hypophosphorous acid. The bismuth remains in solution, and can be subsequently precipitated by a fresh addition of hypophosphorous acid. To the dilute hydrochloric solution of the salts of mercury and bismuth, we add an excess of a solution containing one drop of commercial hypophosphorous acid for each c.c. of peroxide of hydrogen. After standing for an hour the mercurous chloride is filtered off and quickly washed with dilute hydrochloric acid, then with distilled water, after which it is dried at 105° C. The filtrate is heated and made slightly alkaline with caustic soda. We then add the hypophosphorous acid and heat the solution while constantly stirring, until a black precipitate is formed and the liquid becomes clear. The bismuth is filtered off in a Gooch crucible, and washed first with water, then with alcohol, and dried at 105° C. —*Berichte.* xxxi. [2], p. 129.

NOTES AND QUERIES.

*** Our Notes and Queries column was opened for the purpose of giving and obtaining information likely to be of use to our readers generally. We cannot undertake to let this column be the means of transmitting merely private information, or such trade notices as should legitimately come in the advertisement columns.

Synthesis of Ethyl Alcohol.—(Reply to Frank Wood).—In reply to your enquiry (Chem. News, lxxviii., p. 308), you will find the original statement of Berthelot in the *Comptes Rendus*, l., p. 806, and liv., p. 515, that acetylene forms ethylene. The whole subject is discussed in "Die Metallcarbide und ihre Verwendung," von Professor Dr. Felix B. Ahrens, Stuttgart, 1896.—W. G. Brown, Missouri State University, Columbia, Missouri, U.S.A.

MEETINGS FOR THE WEEK.

Monday, 30th.—Society of Arts, 8 (Cantor Lectures). "Bacterial Purification of Sewage," by Dr. Samuel Rideal.

Tuesday, 31st.—Royal Institution, 3. "The Morphology of the Mollusca," by Prof. E. Ray Lankester, M.A., LL.D.

—— Society of Arts, 8. "The Centenary Exhibition of Lithography," by E. F. Strange.

Wednesday, Feb. 1st.—Society of Arts, 8. "The Cost of Municipal Enterprise," by Dixon H. Davies.

Thursday, 2nd.—Royal Institution, 3. "Tibet and the Tibetans," by A. Henry Savage Landor.

—— Chemical, 8. "Maltodextrin, its Oxidation Products and Constitution" and "On Attempts to prepare Pure Starch Derivatives through their Nitrates," by H. T. Brown, LL.D., F.R.S., and J. H. Millar. "An Isomeride of Amarine," by H. Lloyd Snape, D.Sc., Ph.D., and Arthur Brooke, Ph.D. "Propylbenzenesulphonic Acids," by G. T. Moody, D.Sc. "Derivatives of Dibenzylmesitylene," by W. H. Mills and T. H. Easterfield. "On the Action of Chlorosulphonic Acid on the Paraffins and other Hydrocarbons," by S. Young, D.Sc., F.R.S. "The Preparation and Properties of Nitrogen Iodide"; "The Action of Light upon Nitrogen Iodide"; "The Action of Alkaline Hydrates, of Water, and of Hydrogen Peroxide upon Nitrogen Iodide"; "Theory of the Formation and the Reactions of Nitrogen Iodide," by F. D. Chattaway, M.A., and K. J. P. Orton, M.A. "The Action of Reducing Agents on Nitrogen Iodide"; "The Action of Acids upon Nitrogen Iodide," by F. D. Chattaway, M.A., and H. P. Stevens, B.A. "The Composition of Nitrogen Iodide," by F. D. Chattaway, M.A.

Friday, 3rd.—Royal Institution, 9. "The Roman Defences of South-East Britain," by Victor Horsley, M.B., B.Sc., &c.

Saturday, 4th.—Royal Institution, 3. "Brahms" (with Musical Illustrations), by Sir Alexander C. Mackenzie, Mus. Doc.

BERICHTE DER DEUTSCHEN GESELLSCHAFT Wanted, from 1868 to 1879 inclusive.—Address, F.W.R., 2, Farcliffe Place, Bradford.

Wanted, Chief Chemist and Manager of Works by a leading London firm of Manufacturing Chemists employing several hundred people. The qualifications necessary for the position are high and well grounded scientific knowledge and attainments, good practical experience in carrying out manufacturing processes, exceptional powers of organisation and administration, tact, good judgment, capability to direct and control scientific workers engaged in the manufacture of fine Medicinal Chemicals and Pharmaceutical Products. A gentleman with University Training and Degrees preferred. The position commands a liberal salary. Replies will be treated in the strictest confidence if so desired.—Address, stating age, qualifications, and experience, to "Manager," care of Messrs. Markby, Stewart, and Co., 57, Coleman Street, London.

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THE CHEMICAL NEWS.

VOL. LXXIX., No. 2045.

THE PREPARATION AND SOME OF THE PROPERTIES OF PURE ARGON.*

By WILLIAM RAMSAY, F.R.S., and MORRIS W. TRAVERS.

(Concluded from p. 39).

Density of Argon.

FOR a preliminary determination of the density of the various samples a bulb of about 33 c.c. capacity was employed. It is much easier to ensure the purity of a small sample of gas than of a large one; and it will be seen that very concordant determinations are obtainable with a small quantity. The limit of error is probably not greater than one part in a thousand. The results are expressed in terms of O = 16.

	Capacity of bulb. C.c.	Temp.	Pressure. M.m.	Weight. Grm.	Density.
1.	32·762	19·05°	535·1	0·03786	19·65
2.	,,	15·70	712·0	0·05265	19·95
3.	,,	17·00	662·2	0·05012	19·95
4.	,,	14·55	749·8	0·05460	19·91
5.	,,	15·60	740·4	0·05389	19·97
6.	,,	16·15	760·2	0·05501	19·95

The spectrum of No. 4, examined later, showed a trace of nitrogen; the density of No. 6 was confirmed by other two determinations, each made after further sparking.

No. 1 was the first portion boiled off, and therefore its density is lower than that of the other fractions, probably owing to its still containing some neon and helium. The rest of the samples have a constant density, approximately 19·95.

A larger quantity of No. 5 was then purified by long-continued sparking, and its density was determined in a bulb of greater capacity. To show the influence of such purification results are given, obtained before it was complete. The gas under such conditions showed a trace of the nitrogen spectrum. The portion last weighed was spectroscopically pure.

Capacity of bulb. C.c.	Temp.	Pressure.	Weight.	Density.
163·19	15·47°	767·1	0·27235	19·935
,,	16·97	764·8	0·26985	19·914
,,	13·34	742·8	0·26591	19·952
,,	12·95	741·3	0·26586	19·961

After the first of these determinations the gas was passed over a mixture of red-hot magnesium and lime, and subsequently over red-hot copper oxide, in order to remove hydrogen. But after determining the density, the gas was examined spectroscopically, and was found to contain hydrogen. The gas was therefore again sparked, when the density 19·952 was found. This specimen was also examined spectroscopically, and was found to be absolutely free from all visible traces of impurity. The last weighing refers to the same sample of gas, and was made as a control experiment.

These results conclusively prove that the density of argon, purified from its companions, does not differ greatly from that obtained by Lord Rayleigh, viz., 19·94, nor by one of us, viz., 19·941. The true density may, we think, be safely taken as the mean of the last two determinations, viz., 19·957.

This corresponds with the mean of the four reliable determinations with the small bulb, viz., Nos. 2, 3, 5, and 6, which is 19·955.

Refractivity of Argon.

The refractivity of pure argon was next determined. The measurements were made according to the plan suggested by Lord Rayleigh (*Roy. Soc. Proc.*, vol. lix., p. 201). The samples investigated were Nos. 1, 2, 5, and 6. The comparison was made with air.

1. 0·9620 Contains neon and helium.
2. 0·9687
5. 0·9647. Mean, 0·9665.
6. 0·9660.

The refractivity of a previous sample of argon, obtained from the middle of the 15 litres, during the second liquefaction, was 0·9679, a number differing only slightly from that given above.

The refractivity of argon containing krypton, which had a density 20·01, was much higher than the number given above for pure argon, for it reached 1·030 as a mean of two determinations. Evidently then the body possessing the high refractivity was not present in No. 6 in greater proportion than in No. 2, otherwise the refractivity of No. 6 would have shown an increase over that of No. 2.

The refractivity of pure argon differs somewhat from the value for crude argon found by Lord Rayleigh, viz., 0·961 (*Roy. Soc. Proc.*, vol. lix., p. 205), and also from that previously found by ourselves, 0·9596. The removal of neon, which appears to have a very low refractivity, and of helium, of which the refractivity is 0·1238, accounts for the increased refractivity of a sample from which they are absent. The gases which we have recently found in air and in crude argon will form the subject of a future communication. Suffice it to say that the amount of neon and helium is much more considerable than that of the others, and that their effect on crude argon is, therefore, much more marked on its density and refractivity.

To revert to the opening sentences of this communication, we may point out that the remarks on the homogeneous nature of argon were just at the time. The change in its physical constants, caused by the mixture of more recently discovered gases which it has been shown to contain, is exceedingly small, and does not call for any serious alteration in the original paper on "Argon, a New Constituent of the Atmosphere."

The Density of Argon at the Boiling Point of Oxygen.

In an addendum to the original paper on Argon (*Phil. Trans.*, A, 1895, p. 239), the expansion of argon by rise of temperature to 250°, as well as its contraction by fall of temperature to −88°, was determined. There is a considerable difference between the temperature at which nitrous oxide boils and that at which oxygen boils, and it was thought worth while to ascertain whether argon behaves as a normal gas down to the boiling point of oxygen. Olszewski (*loc. cit.*, p. 257), gives the boiling point of argon as −187°, and that of oxygen as −182·7°; at the latter temperature, therefore, argon would not be far removed from its own condensing point. The interesting question, of course, is the possible polymerisation of argon at such a low temperature.

No sign of any polymerisation has been observed, as is shown by the following data:—

Hydrogen Thermometer.

Temperature. °C.	Pressure. m.m.	Volume.	R.
99·7	1091·5	1·0026	2·9362
0·0	803·2	1·0000	2·9121
−182·7	269·6	0·9953	2·9715

Argon Thermometer.

100·1	1414·9	1·0026	3·8095
0·0	1040·0	1·0000	3·8022
−182·7	353·2	0·9953	3·8930

* A Paper read before the Royal Society, December 15, 1898.

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No correction has been made for the unheated or uncooled stem of the thermometer; but it is obvious that although the lowest temperature lies close to the boiling of argon, the ratio of the values of PV/T of hydrogen and argon at that temperature, as well as the others, is practically constant.

ON THE

ESTIMATION OF CARBON AND HYDROGEN IN VOLATILE ORGANIC LIQUIDS.

By F. W. STREATFEILD, F.I.C., and LEWIS EYNON.

It is well known that, in the estimation of carbon and hydrogen in liquids that boil or vapourise at a low temperature, many practical difficulties are met with. When the substance contained in a glass bulb is manipulated within the combustion-tube very great care must be taken to prevent too rapid expulsion of the liquid from the bulb, otherwise failure results from incomplete combustion and backward diffusion. Again, when the substance is contained in a small sealed tube outside the combustion-tube, a great deal of experience and dexterity is required in breaking the ends of the tube and preventing loss.

Having occasion recently to undertake the estimation of the constituents of some volatile organic liquids, we have devised the following little apparatus, which, we believe, will greatly simplify operations of the kind here under consideration. Reference to Fig. 1 will, we hope, render the construction of the apparatus evident.

It consists of a moderately large test-tube, preferably made from thick glass tubing fitted with a caoutchouc stopper pierced with three holes. Through one of these a glass tube passes; this is connected with the air or oxygen supply, and just dips under the surface of some mercury placed in the tube. Another glass tube connects the apparatus with the combustion tube. The third hole carries a glass rod bent over or flattened at one end. The glass rod may be made to slide in a glass tube, supported and made air-tight by a piece of well-fitting caoutchouc tubing, as shown in the sketch.

The method of using the apparatus requires little or no explanation. The substance, contained in a sealed thin glass bulb, is placed in the test-tube, the stopper inserted, and the apparatus connected to the combustion-tube. Everything being in order, the glass tube is broken by pressing down the rod, and the vapour slowly and carefully expelled by the current of air or oxygen. Towards the end of the operation the apparatus may be surrounded with hot water contained in a beaker. It will be seen that, by means of the mercury trap, there is little or no possibility of the vapour of the substance diffusing backwards, and if the current of air be carefully regulated complete combustion results, provided, of course, there is a good length of copper oxide in the combustion-tube.

In cases where, owing to the nature of the vapour, the caoutchouc fittings may be attacked, we propose the following modification (see Fig. 2): it consists, as will be seen, in simply inverting the test-tube and bending the air-supply tube over on itself, so that the end of the tube dips under the surface of the mercury which covers the caoutchouc stopper.

Of course a more elaborate apparatus might be constructed by fusing the entrance and exit tubes into the sides of the test-tubes.

We append the following results obtained with the apparatus in the combustion of petroleum ether:—

	Carbon.	Hydrogen.	Total.
1.	83·57 per cent	16·44 per cent	100·01 per cent
2.	83·337 ,,	16·578 ,,	99·915 ,,

We regret that we are unable to publish further results as unfortunately our work has been interrupted. We

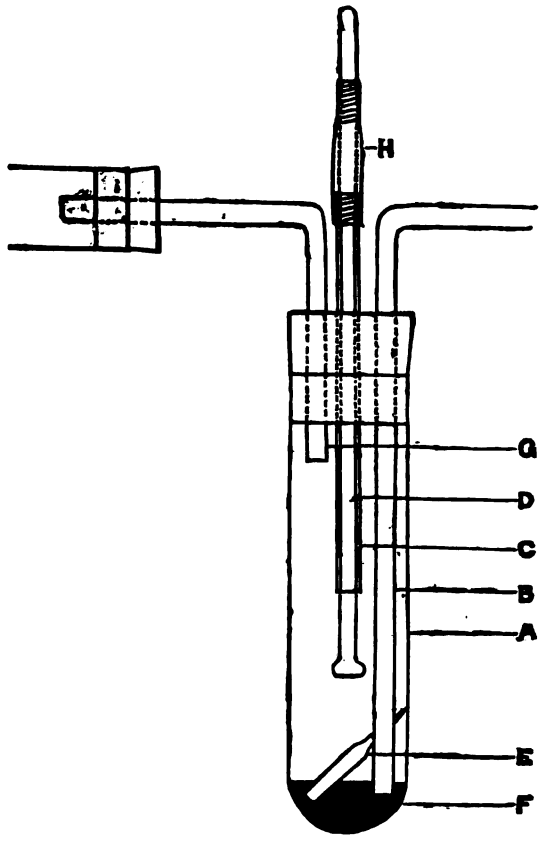

FIG. 1.

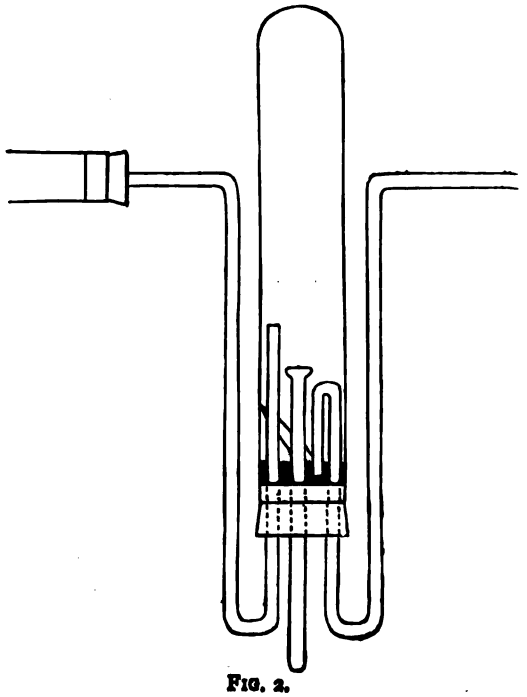

FIG. 2.

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venture, however, to submit the foregoing, incomplete as it is, hoping it may be sufficiently interesting and suggestive to induce others to experiment with our apparatus.

City and Guilds Technical College,
Finsbury, E.C.

APPARATUS FOR THE SAPONIFICATION OF FATS, OILS, &c.

By J. G. ANNAN.

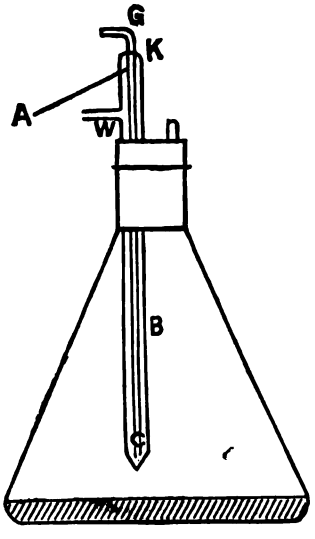
Having had a number of oils to examine lately, I devised the following convenient arrangement for carrying out the preliminary saponification necessary in some of the determinations:—

A small condenser is made according to figure A of accompanying sketch.

B is a tube of about §ths inch bore and about 5 inches long, with a side tube blown at W and a central tube of about ⅛th inch bore C C jointed or passed through a cork at K.

An Erlenmeyer flask of any convenient size is taken and fitted with a cork perforated with two holes, one to carry the condenser, the other to be closed by a piece of glass rod.

Introduce the weighed fat and measured quantity of alcoholic potash, insert the cork carrying the condenser, but leave the small hole open. Connect the condenser



with the water supply and place the flask over a small flame. When, by gentle boiling, the air is considered to be displaced from the flask, insert the glass rod, and at the same time turn on the water.

The gas may now be turned up to boil the liquid vigorously, and the apparatus may be left without further attention until the saponification is considered to be complete, when the glass rod may be withdrawn and the gas turned out.

Amongst the first experiments made the end of a small manometer was inserted into the open hole instead of a glass rod, in order to observe variations in pressure. Through many considerable variations of flame the internal pressure remained practically the same as the atmospheric pressure.

It is evident that this apparatus has some advantages over that generally used for saponifications, more especially in the determination of Koettstorfer's figure.

CERTAIN ALKALOIDAL PERIODIDES, AND THE VOLUMETRIC ESTIMATION OF ALKALOIDS AS HIGHER PERIODIDES.*

By A. B. PRESCOTT and H. M. GORDIN.

(Concluded from p. 47).

Application in Assay of Crude Medicinal Drugs.

We have made estimations of total alkaloids in nux vomica, and in belladonna, by the periodide volumetric method, after extraction of the alkaloid in several ways, and have obtained satisfactory results. We have work in hand by which we hope to reach more expeditious methods of extraction. Among the menstrua under experimentation are a saturated solution of gaseous ammonia in ether, a chloroformic solution of ammonia (suggested by Siedler and Thomas, *Ber. d. Pharm. Ges.*, 1898, 28), and similar agents.

A Volumetric Assay of Opium.

The morphine was estimated as periodide, after successive treatment with benzol, amyl alcohol or acetone, and lime-water.

This method proceeds upon the following plan:—The opium alkaloids are set free by action of ammonia with certain solvents. The free narcotine, papaverine, codeine, and thebaine are then removed by percolation with benzene, after which the morphine is taken out by percolation with acetone,† in which the morphine is sufficiently soluble. The acetone is then evaporated off, and the residue taken up with lime-water, which completely dissolves and purifies the morphine. It remains to filter the lime solution, acidulate it with hydrochloric acid, and estimate the morphine as periodide by titration as already detailed in this paper.

In the percolation of the opium with different solvents to separate the morphine, we depend upon two things, (1) the preparing of the opium powder by digestion with the ammonia and the solvents and then drying, and (2) an admixture with dry common salt in transferring to the percolator.

The Materials for the Assay.—Opium in fine powder (No. 60 or finer), 1 grm.; stronger ammonia water; alcohol, ether, chloroform, pure benzene (crystallised); acetone, boiling between 54° and 58° C., and about 200 c.c.; some good lime-water; ordinary common table salt, about 20 grms.; some diluted hydrochloric acid (10 per cent); decinormal solution of iodine with potassium iodide (Wagner's reagent), and sodium thiosulphate solution standardised with the solution of iodine.

Directions for the Assay.—Of the opium in fine powder one grm. is weighed into a small mortar or deep dish, such as can be well covered with admission of a small pestle.‡ A mixture is made of 5 c.c. of stronger ammonia water, 5 c.c. of alcohol, 20 c.c. of ether, and 10 c.c. of chloroform. The opium is rubbed up with 2 or 3 c.c. of this mixture, to make a uniform paste, using a pestle that can be left in the dish when it is covered. The covered dish is now put aside for about three hours, from time to time moving the dish gently; about 15 grms. of well dried and finely powdered common salt are now added and carefully mixed into the mass. Then the dish is left open in a warm place, of 30° to 35° C., for two or three hours, when it is placed in a desiccator containing sulphuric acid and a dish of paraffin, a vacuum desiccator being preferable, until the mixture is perfectly dry, as shown by the looseness of the powder under the motion of the pestle. If left over night it is sufficient. The entire contents of the dish are now transferred to a little

* *Journal of the American Chemical Society*, xx., No. 9, Sept., 1898.

† Instead of acetone there may be used pure amyl alcohol, boiling between 128° and 132° C., and leaving no residue upon evaporation below the boiling-point.

‡ A screw-top ointment jar of mortar-shaped bottom and four or six ounces capacity serves very well.

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glass percolator of about $\frac{1}{10}$ c.m. (one half inch) inner diameter, and 22 c.m. (9 inches length,* rubbing out the dish twice with a little more of the dried common salt. The mass is now percolated with the benzene, until the percolate is colourless, and until upon evaporating 1 or 2 drops of the percolate in a watch-glass, taking up the residue with 4 or 5 drops of acidulated water, and adding a drop or two of Wagner's reagent, no turbidity appears (removal of alkaloids other than morphine). A shallow dish is now set under the percolator, and pure acetone used to continue the percolation to complete exhaustion, as found by evaporating 10 drops of the percolate on a watch-glass, taking up the residue with 2 or 3 drops of acidulated water, and adding a drop or two of Wagner's reagent, when no turbidity at all should appear. Usually as much as 200 c.c. of acetone are required. The acetone is now evaporated, at a temperature not exceeding 45° C., to complete dryness. The residue when cool is rubbed up with good fresh lime-water, the solution poured without filtering into a graduated stoppered cylinder of 100 c.c., the dish washed four or five times with portions of lime-water, to fully clean the dish, when lime-water is added to make the volume 100 c.c. The cylinder is now securely stoppered and well shaken for half an hour. Of the mixture enough is now filtered into another graduated cylinder, with glass stopper, to make up a filtrate exactly 50 c.c. To this liquid is added diluted hydrochloric acid (10 per cent) to just perceptible acidulation, and the tenth-normal iodine solution is slowly run in from the burette while gently shaking the cylinder until precisely 25 c.c. have been added. Water is added to any convenient mark of the cylinder, which is then stoppered securely and shaken vigorously and continuously (for about twenty minutes) until, on standing a minute or two, the supernatant liquid (of a pronounced iodine-red colour)† is perfectly clear and transparent. The liquid is now filtered off so as to take just one-half the volume of the filtrate. In this half of the liquid the excess of iodine is titrated back with the tenth-normal sodium thiosulphate solution, using starch as an indicator. The number of c.c. of the thiosulphate solution multiplied by 2, is subtracted from 25, the number of c.c. of iodine solution used. The remainder is now multiplied by the factor 1·89586 (0·0094793 × 2 × 100), the product being the percentage of morphine in the powdered opium as weighed.

The precautions most essential are (1) that the opium residue before percolation be thoroughly dried, (2) that acetone should not contain anything distilling below 54° C., or above 58° C., and (3) that after the added excess of iodine the container be continuously shaken until the precipitate is so fully separated that the solution above it is clear. An automatic shaker is an aid in this assay. A second estimation can be made with the remaining part of the lime solution.

Without the use of lime-water in purification of the morphine of the residue, we find the colour of the resulting acidulous solution to be inconvenient in the titration, and find the percentage figure to be uniformly higher than when obtained after lime solution. The vessel is easily cleaned from adhering morphine periodide by the use of acetone.

Results of the Opium Assay by the Periodide Method.

We can give here the results of assays of but 3 samples of powdered opium, these coming from three different reputable houses. They were all marked, sample A to contain 14 per cent, samples B and C to contain the quantity required by the U. S. P. Three analyses of each sample were made, and to sample A the U. S. P. method was also applied, and was found to contain 14·4 per cent morphine by that method. The volumetric method was carried out exactly as described above.

	Opium taken in grms.	Iodine consumed by one-half.	Percentage morphine found.
Sample A.			
1	1·0036	0·116644	17·41
2	1·008	0·116732	17·37
3	1·0022	0·116642	17·44
Sample B.			
1	1·0033	0·08872	13·25
2	1·0023	0·08872	13·20
3	1·0026	0·08872	13·21
Sample C.			
1	0·9969	0·096319	14·48
2	1·0016	0·097219	14·55
3	0·9988	0·094552	14·19

As a Valuation of the Morphine of any Pharmacopœial Assay.

If it should be desired to estimate the alkaloid in the crystals obtained in assay by the pharmacopœia of this or any other country, the periodide volumetric analysis could be well applied as follows:—

Let the crude morphine obtained by the pharmacopœial method be taken up with lime-water, the latter made up to a given volume, and a measured portion of the filtered solution, placed in a graduated vessel and acidulated with hydrochloric acid; let a definite excess of the decinormal iodine be added, in small portions at a time, and shaken after each addition, till the periodide separates out, and the clear liquid retains a dark red colour, making up the mixture to a given volume; filtering off half and then titrating the excess of iodine in this half by standard sodium thiosulphate, the amount of iodine consumed can be easily found. Working on 10 grms. opium, a tenth portion of the lime-water solution would represent 1 grm. of opium, and the percentage of morphine would be equal to the weight of iodine consumed, multiplied by 74·918, or to the number of c.c. of the tenth-normal iodine consumed, multiplied by 0·94793. Several analyses could be made with the remaining part of the lime-water solution.

ON THE CAUSE OF THE RETENTION AND RELEASE OF GASES OCCLUDED BY THE OXIDES OF METALS.*

By THEODORE WILLIAM RICHARDS.

(Continued from p. 43).

Hypothetical Explanation.

THE facts are now perfectly clear, and it remains only to account for them by means of a plausible theory. In the first place, there can be no question that the gases proceed from a residue of basic nitrate imprisoned in the oxides in question; the fact that oxides prepared from the carbonates contain little or no gas would alone be sufficient support for this point of view. The first matter to be considered is, then, the dissociation of this residual nitrate, which is probably wholly analogous to that of calcic carbonate as studied by Le Chatelier (*Compt. Rend.*, 1886, cii., 1243; Nernst, *Theoret. Chem.*, 1894, p. 377). We may express this reaction, perhaps, in the following fashion, which indicates that the proceeding is supposed to take place in the gaseous phase, while the solids enter into the reaction solely by their vapour tension.

* The tube of a one-ounce syringe does very well.

† If the liquid does not have this red colour, it must be because of a lack of the indispensable excess of the iodine, of which an additional quantity should be added.

* Contributions from the Chemical Laboratory of Harvard College. From the *Proceedings of the American Academy of Arts and Sciences*, xxxiii., No. 22; also *American Chemical Journal*, November, 1898.

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$$\underset{\text{Vapour.}}{Cu(NO_3)_2.3CuO} \rightleftharpoons \underset{\text{Vapour.}}{4CuO} + [N_2O_5]$$

$$\downarrow\uparrow \qquad\qquad \downarrow\uparrow$$

$$\underset{\text{Solid.}}{Cu(NO_3)_2.3CuO} \qquad \underset{\text{Solid.}}{4CuO}$$

It is probable that Graham's basic cupric nitrate $Cu(NO_3)_2.3Cu(OH)_2$ is dehydrated before the nitric acid begins to leave; if it is not, of course 3 molecules of water must be added to the products above. The addition of the water does not affect the essential point in the following logic, however. The gaseous products of this reaction attain a pressure of 760 m.m. at about 280°.

The reaction represented above is evidently only a preliminary stage of the whole change; it may have scarcely begun, or may have run almost to an end in some cases before the dissociation of the nitric anhydride begins to enter into the problem. This dissociation may be complete, resulting in a mixture of the elementary gases, or it may (and does at ordinary pressures) stop at one of the lower oxides of nitrogen. Since the gases, whatever they may be, are necessarily held in microscopic cells, while their own volume under ordinary pressure is several times that of the total volume of the solid containing them, it is obvious that the pressure under which they exist must be very great. At this great pressure the stability of N_2O_5 must be very considerably increased, for the reaction $2N_2O_5 = 2N_2 + 5O_2$ is one which pressure must seriously affect, because of the change of volume concerned in it; but more probably the peroxide of nitrogen may be the first product of the reaction. In any event, it is evident that the complete separation of the oxygen and nitrogen does not take place immediately, for much less nitrogen was yielded by the specimens of each oxide heated for a short time at comparatively low temperatures than by like specimens heated longer or hotter.

Both of these reactions, the decomposition of the cupric nitrate as well as that of the oxides of nitrogen, evidently, then, require time for their completion, so that the maximum of gas contents is not immediately attained. Besides being accelerated by heat, they are also possibly both hastened by the escape of a portion of the oxygen, an interesting phenomenon which occurs side by side with the decomposition. To make the matter clearer, let us represent the dissociation of the oxide of nitrogen by the general formula $2NO_x = N_2 + xO_2$. The speed of this reaction is represented by the equation—

$$-\frac{dc}{dt} = k c^2 - k^1 c_1 c_2^x,$$

an expression which increases in magnitude as c_2 (the concentration of the oxygen) diminishes. Since it is probable that k^1 is very small,—that the chief tendency of the reaction is from left to right,—this cause of acceleration is not an important one. In a similar way the decomposition of the oxides of nitrogen likewise accelerates the more complex reaction into which the solids enter.

In every case this decomposition of the oxides of nitrogen, and therefore that of the cupric nitrate, had nearly advanced to completion before the oxygen had all been expelled. This led to the existence of a maximum of gas volume after a brief heating, a maximum less marked in the case of cupric oxide than in the other cases, because the extra oxygen escapes from cupric oxide almost as fast as it is formed. Thus many of the apparent eccentricities in the behaviour of the gases find a simple and adequate explanation. The numerous results with different oxides were sought in the hope that the relations might be capable of quantitative proof according to the law of mass action, as well as of qualitative demonstration, but the great number of possible compounds and reactions made this hope vain.

It remains only to devise an hypothesis to explain perhaps the most interesting phenomenon under discussion, to show why the oxygen is capable of escaping more rapidly than the nitrogen. Obviously diffusion or transpiration cannot account for this; for any orifice, no matter how small, which would allow the oxygen to escape, must also allow the nitrogen to escape. The only possible explanation is the supposition that the oxygen finds its way out chemically, by uniting with metal or a lower oxide which has momentarily released some of its proper supply of oxygen. The displaced gas, being forced to find another berth, presently in its turn occupies the place of still another portion, and so on, until most or all of the excess has found its way out of prison. Of course the nitrogen cannot use this means of escape, for it is not surrounded by a compound which yields it upon dissociation; the nitrogen can only escape through holes originally present or formed by the re-arrangement of the substance of the solid.

This hypothesis suggests Grotthus's obsolete explanation of electrolysis, or rather that of Clausius; for the most plausible conception is that in the hot rapidly-vibrating solid a portion of the oxygen which ought to be combined with the metal is always in a free state, and that this condition, by a recurring process of dissociation and association, permits relieving the high pressuure of the oxygen in the cell. It is possible that water occluded in the oxide may play the part of a go-between, but there is no experimental evidence of this. It is no new idea to explain the diffusion of hydrogen through palladium, or of carbon through iron in the cementation process, and other similar phenomena, by a similar mechanical conception.

Quite in accord with this point of view are a number of facts. In the first place cupric oxide, the most easily reducible of the oxides investigated, parts with its occluded oxygen with the greatest ease, at the same time obstinately retaining the nitrogen. The progressive increase in the tendency to retain oxygen in the cases of zinc and magnesium corresponds to the increase in the difficulty of reducing these oxides. In other words, the least stable oxide is the one which has the feeblest hold upon the occluded oxygen. Cupric oxide begins to lose this impurity with great rapidity at 520°, zincic oxide loses it less rapidly even at 750°, and magnesic oxide is still more obstinate. It is probable, moreover, that in the cases of zinc and magnesium there is a slight amount of transpiration, for a small part of the nitrogen was found to leave at the higher temperatures. This transpiration ought to assist the oxygen also to escape, although in somewhat less measure than the nitrogen; but in spite of this possibility of more rapid escape, the oxygen is still held more firmly than in the case of cupric oxide. In this latter substance all the *nitrogen* is retained indefinitely at temperatures below 850°, forming the constant gas residue noted in the first experiments; only when the definite structure of the oxide is broken up, and the dissociation tension of the cupric oxide becomes so great that cuprous oxide begins to be formed, does the nitrogen take its flight. On the other hand, a reducing atmosphere is needed to force zincic oxide to relinquish all its gas, unless an excessively high temperature is employed. Forty-three years ago Sainte-Claire Deville and Rivot showed that at a red heat such an equilibrium exists between zincic oxide, zinc, hydrogen, and water, as to enable zinc oxide to be sublimed in a current of hydrogen, the dissociated oxide re-forming when cooled (*Am. Chem. Phys.*, [3], xliii., 7, 477). This reaction undoubtedly enables the occluded gas to escape, by destroying the structure of the solid when gases from the flame are present.

Again, the fact that many solids, the oxides in question among them, manifest upon heating the peculiar contraction called "sintering," is evidence of the existence of molecular instability and possibility of re-arrangement. The hypothesis of partial dissociation at high temperatures is adequate to explain this.

(To be continued).

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PROCEEDINGS OF SOCIETIES.

CHEMICAL SOCIETY.

Ordinary Meeting, January 19th, 1899.

Professor Dewar, F.R.S., President, in the Chair.

Messrs. W. Ackroyd, E. M. Rich, and C. W. T. Woods were formally admitted Fellows of the Society.

Certificates were read for the first time in favour of Messrs. Robert Alfred Bolam, 31, Oxford Street, Newcastle-on-Tyne; James Washington Epps, 95, Upper Tulse Hill, S.W.; Ernest Barratt Fairweather, King's College Hospital, Lincoln's Inn Fields, W.C.; Colin Charlwood Frye, Burwood, Woodville Road, Ealing, W.; Edmund Vivian Gabriel, Bengal United Service Club, Calcutta; Harold Brewer Hartley, Romney Lodge, New Park Road, Clapham Park, S.W.; Tom Lacey Hewitt, Beech Field, St. John's, Higher Broughton, Manchester; Edward Flaxman Linstead, 35, Hayter Road, Brixton Hill, S.W.; Thomas Mackenzie, 8, Gardner Street, Glasgow; Joshua Maudsley, Merchiston Castle, Edinburgh; Arthur Mirrlees, Redlands, Kelvinside, Glasgow; Bernhard Mohr, 69A, Parliament Hill, Hampstead, N.W.; John Cavendish Molson, 42, Sackville Road, Hove, Brighton; John Trengove Nance, District Bank, Newcastle, Staffs.; William Walker Scott Nicholls, 230, Brockley Road, Brockley, S.E.; Horace Seymour Pyne, Castletown, Isle of Man; Arnold Stevenson, 4, Porchester Gardens, S.W.; Henry Fox White, Warnham, Woodland Road, Clifton, Bristol.

Of the following papers those marked * were read:—

*1. "*Researches on Moorland Waters. I. Acidity.*" By William Ackroyd, F.I.C.

Moorland waters are consumed by over five and a quarter millions of people in England. The quality of acidity possessed by these waters, which has been associated with plumbo-solvent action, is therefore of great importance. The author differentiates between organic and inorganic acidity, and describes a method for ascertaining their amounts which consists of—(1) titration with N/100 alkali, using phenolphthalein as indicator, and (2) aspiration of air free from carbon dioxide through another portion, and a second titration for the residual acidity. The precautions to be used are described.

Data are given showing the loss of acidity due to diffusion in observations extending over 181 days. Comparisons are made proving that the differences in acidity of waters from various gathering grounds are due to differences of gradient. It is finally shown that the organic acid in solution, always assumed to be humic acid, is of lower equivalent than that of the lowest humic acid known.

Discussion.

The President said that the plumbo-solvent action of the water supplied to Sheffield, Bradford, and Huddersfield, has been overcome by the addition of finely precipitated carbonate of lime in the reservoirs, with the result that the quality of the water was improved, not only by removal of the acidity, but also indirectly by precipitation of the dissolved peaty matter.

*2. "*Esterification Constants of Substituted Acetic Acids.*" By John J. Sudborough and Lorenzo L. Lloyd.

Goldschmidt has shown (*Ber.*, 1895, xxviii., 3218) that the esterification of an organic acid in the presence of a catalytic agent, such as hydrogen chloride and of a considerable excess of alcohol, may be regarded as a monomolecular reaction, and may, therefore, be represented by the equation—

$$\frac{dx}{dt} = K(a-x),$$

which, on integration, gives—

$$K = \frac{1}{t}\log_e \frac{a}{a-x};$$

where a is the initial concentration of the acid, $a-x$ the concentration of the acid after time t, and K the esterification constant. According to Goldschmidt, and also according to experiments made by the authors, K is directly proportional to the amount of hydrogen chloride present when dilute solutions are employed. In all cases K is calculated for normal hydrogen chloride.

The authors suggest that the letter E be used for the esterification constant, as K is already employed to denote the dissociation constant of an acid. E would then represent the esterification constant of an acid when normal hydrogen chloride is used, and E 10°/EtOH would represent the esterification constant of an acid with ethylic alcohol and a normal solution of hydrogen chloride at a temperature of 10°.

In the authors' experiments, N/40 hydrogen chloride was employed, and the organic acid was practically N/10 in all cases. Equal volumes of N/5 solutions of the acid in 100 per cent ethylic alcohol, and of N/20 hydrogen chloride in 100 per cent alcohol, were mixed, and 30 c.c. of the mixture run into small stoppered bottles, and maintained at a temperature of 14·5°. The contents of these bottles were then titrated with N/10, and finally with N/20 alkali, phenolphthalein being employed as indicator. The constants were calculated from the equation, and the results are given in the following table, together with the dissociation constants where known.

Acid.	Formula.	E 14·5°/EtOH.	K.
Acetic	$CH_3{\cdot}CO_2H$	3·661	0·00180
Propionic	$CH_2Me\,CO_2H$	3·049	0·00134
Chloracetic . ..	$CH_2Cl{\cdot}CO_2H$	2·432	0·155
Phenylacetic ..	$CH_2Ph{\cdot}CO_2H$	2·068	
Bromacetic . ..	$CH_2Br{\cdot}CO_2H$	1·994	0·138
Iodacetic	$CH_2I{\cdot}CO_2H$	1·713	0·075
Isobutyric	$CHMe_2{\cdot}CO_2H$	1·0196	0·00144
Trimethylacetic .	$CMe_3{\cdot}CO_2H$	0·0909	0·000978
Dichloracetic ..	$CHCl_2{\cdot}CO_2H$	0·0640	5·14
Diphenylacetic ..	$CHPh_2{\cdot}CO_2H$	0·05586	
Dibromacetic ..	$CHBr_2{\cdot}CO_2H$	0·0510	
Trichloracetic ..	$CCl_3{\cdot}CO_2H$	0·0372	121·0
α-Bromisobutyric .	$CMe_2Br{\cdot}CO_2H$	0·0356	
αα-Dibromopropionic	$CMeBr_2{\cdot}CO_2H$	0·0242	3·3
Tribromacetic ..	$CBr_3{\cdot}CO_2H$	0·01345	

It thus appears that the rate of esterification depends on the constitution of the acid rather than on its strength. The authors are engaged in determining the esterification constants of substituted acrylic acids, and hope to extend the work to other series.

*3. "*Diortho-substituted Benzoic Acids.* Part IV. *Formation of Salts from Diortho-substituted Benzoic Acids and different Organic Bases.*" By Lorenzo L. Lloyd and John J. Sudborough.

In continuation of their work on diortho-substituted benzoic acids (*Trans.*, 1895, lxvii., 588 and 601; 1897, lxxi., 229), the authors have attempted to prepare salts from 2 : 4 : 6-trinitrobenzoic, 2 : 4 : 6-tribromobenzoic, 2 : 4 : 6-tribromo-3-aminobenzoic, metanitrobenzoic, and benzoic acids, and the following bases:—Trimethylamine, tripropylamine, tribenzylamine, diethylaniline, aniline, metabromaniline, metanitraniline, 2 : 4 , and 2 : 6-dibromaniline, pseudocumidine, mesidine, diphenylamine, and α- and β-naphthylamines, with results which are described in the paper. The investigation was undertaken in order to determine whether the capacity to form salts is dependent on (1) the strength of the acid and of the base, or (2) the constitution of the acid and of the base, or on both of these.

It was thought probable that a tertiary base of high molecular weight might not be able to combine with a diortho-substituted acid, but the reverse has proved to be

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the case. Bases such as tribenzylamine, metanitraniline, &c., which will not combine with benzoic acid, readily combine with such diortho-substituted derivatives as 2 : 4 : 6-trinitrobenzoic, 2 : 4 : 6-tribromobenzoic, and 2 : 4 : 6-tribromo-3-aminobenzoic acids. This behaviour can only be accounted for by the fact that these are much stronger acids than benzoic, and combination between substituted benzoic acids and different bases would, therefore, appear to depend entirely on the strength of acid and strength of base.

Combination could not be effected between benzoic acid and metabromaniline, diethylaniline, pseudocumidine, or tribenzylamine, between metanitrobenzoic acid and tribenzylamine, and between trinitrobenzoic or tribromaminobenzoic acids and 2 : 4- or 2 : 6-dibromaniline, or diphenylamine.

The salts of trinitrobenzoic acid have no well-defined melting-points; when heated, they become dark coloured, then melt and decompose, the temperature at which this occurs depending on the mode of heating. Most of the other salts have well-defined melting-points.

*4. "*α-Ketotetrahydronaphthalene.*" By F. Stanley Kipping, D Sc., F.R.S., and Alfred Hill.

The reaction involved in the synthesis of α-hydrindone from phenylpropionic chloride by means of aluminium chloride (*Trans.*, 1894, lxv., 480) is probably capable of wide application, and the authors have commenced experiments recently with the object of studying its usefulness in various directions. It has been found that when phenylbutyric chloride is treated with aluminium chloride under suitable conditions, it is converted into α-ketotetrahydronaphthalene by intramolecular condensation,

$$C_6H_5\cdot CH_2\cdot CH_2\cdot CH_2\cdot COCl = C_6H_4\begin{<}{CH_2\cdot CH_2}{CO\cdot CH_2}\end{>} + HCl;$$

a reaction which is exactly analogous to that by which α-hydrindone is prepared.

α-Ketotetrahydronaphthalene is a colourless highly refractive liquid, having a slight odour faintly recalling that of both camphor and peppermint. The *semicarbazone*,—

$$C_{10}H_{10}{:}N\cdot NH\cdot CO\cdot NH_2,$$

crystallises from alcohol in yellow needles or prisms, melts and decomposes at 217—220°, and is sparingly soluble in cold alcohol; when heated with dilute hydrochloric acid, it is decomposed, the ketone being regenerated. The *phenylhydrazone*, $C_{10}H_{10}{:}N\cdot NHPh$, crystallises from methylic alcohol in massive transparent plates melting at 84—85°; it is readily soluble in most ordinary solvents and is very unstable in the air. The *parabromophenylhydrazone*, $C_{10}H_{10}{:}N\cdot NH\cdot C_6H_4Br$, separates from alcohol and other solvents in long colourless prisms and melts at 117—118°; it is more stable than the hydrazone, but, like the latter, is decomposed by hot hydrochloric acid, the product being probably analogous to that obtained from the hydrazone of α hydrindone in a similar manner. The *oxime*, $C_{10}H_{10}{:}N\cdot OH$, separates from cold methylic alcohol in very large well-defined rhomboidal crystals; it melts at 102·5—103·5°, and is readily soluble in most ordinary solvents, but insoluble, or nearly so, in water. When reduced with sodium amalgam in acetic acid solution, the oxime is converted into a base, which is doubtless identical with the tetrahydro-α-naphthylamine described by Bamberger and Bammann (*Ber.*, 1889, xxii., 951).

*5. "*A New Method for Preparing Unsymmetrical Dimethyl- and Trimethyl-succinic Acids.*" By William A. Bone.

When ethylic sodiomalonate or ethylic sodiomethylmalonate is treated with ethylic α-bromisobutyrate in alcoholic solution, a mixture of ethylic salts of tricarboxylic acids is obtained. This, on hydrolysis with concentrated hydrochloric acid, yields a mixture of isomeric methyl derivatives of succinic and glutaric acids, in which, however, the glutaric acid very largely preponderates, the yield of the isomeric succinic acid being very small.

This is due to the fact that, in presence of the strongly alkaline solution, the ethylic α-bromisobutyrate readily loses hydrogen bromide, forming ethylic methacrylate, which then condenses with the ethylic malonate, or ethylic methylmalonate, according to the equation—

$$(CO_2Et)_2CH_2 + CH_2{:}CMe\cdot CO_2Et = (CO_2Et)_2CH\cdot CH_2\cdot CHMe\cdot CO_2Et,$$

and the resulting ethereal salt, on hydrolysis with concentrated hydrochloric acid, yields a methyl derivative of glutaric acid.

The author has found that if the sodium derivative of ethylic cyanacetate, which is almost insoluble in alcohol, be heated with an alcoholic solution of ethylic α-bromisobutyrate, the latter apparently does not lose hydrogen bromide, forming ethylic methacrylate, but reacts quite normally with the ethylic sodiocyanacetate, according to the equation—

$$(CO_2Et)(CN)CHNa + BrCMe_2\cdot CO_2Et = (CO_2Et)(CN)CH\cdot CMe_2\cdot CO_2Et + NaBr,$$

and a very good yield of unsymmetrical ethylic dimethylcyanosuccinate is obtained. This, on hydrolysis with concentrated hydrochloric acid, yields practically the theoretical quantity of an acid melting at 139—140°, the composition and properties of which are identical with those of unsymmetrical dimethylsuccinnic acid.

Unsymmetrical ethylic dimethylcyanosuccinate contains a hydrogen atom replaceable by sodium. The sodium compound, which is soluble in alcohol, readily reacts with methylic iodide, yielding ethylic trimethylcyanosuccinate, and this, on hydrolysis with concentrated hydrochloric acid, is converted into trimethylsuccinic acid.

By means of these reactions, unsymmetrical di- and trimethylsuccinic acids can be readily prepared in quantity. It is probable, moreover, that any mono-, di-, or tri-alkyl derivative of succinic acid may be prepared by starting with ethylic cyanacetate, and working on the lines indicated; the author is, therefore, making a special study of these reactions.

6. "*The Production of Optically Active Mono- and Di-alkyloxysuccinic Acids from Malic and Tartaric Acids.*" By Thomas Purdie, F.R.S., and William Pitkeathly, B.Sc.

In continuation of a previous research (*Trans.*, 1898, lxxiii., 287), the authors have made further observations on the production of the ethereal alkyloxysuccinates in the interaction of silver malate and alkyl iodides. Small quantities only of these compounds were formed in the cases examined. A similar abnormal reaction occurs between silver tartrate and isopropylic iodide, an active ethereal salt of di-isopropoxysuccinic acid being found in the product; other alkyl iodides no doubt act in the same manner, though probably to a smaller extent.

The alcoholic hydroxyl groups of ethylic malate and tartrate are readily and completely alkylated by ethylic iodide in the presence of silver oxide. Diethoxysuccinic acid obtained by this method is a crystalline, highly dextrorotatory compound. The observations made on the rotatory powers of this acid and its ethylic, barium, and sodium salts furnish an explanation of the apparently anomalous results obtained by Rodger and Brame in preparing the alkylic tartrates from the silver salt (*Trans.*, 1898, lxxiii., 301).

The method of alkylation by means of alkyl iodides and silver oxide, which does not appear to have been used previously, is generally applicable to the ethereal salts of hydroxy-acids, and probably also to other substances of a similar nature. As racemisation does not occur in the process, it is specially adapted for the preparation of optically active compounds.

7. "*The Action of Ammonia on Ethereal Salts of Organic Acids.*" By Siegfried Ruhemann.

This paper is a continuation of the author's researches on the formation of pyridine derivatives from unsaturated

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acids. The ethylic salts of these acids have been prepared by the interaction of sodium ethoxide with a mixture of the salts of the acids of the malonic series and those containing an acetylene linkage. Ethylic phenylpropenetricarboxylate, on treatment with ammonia is converted into *ethylic γ-phenyl-αα'dihydroxy-β-carboxylate*, crystallising in colourless prisms melting at 200°, and *phenyldihydroxypyridine*,—

$$CPh\leqslant\begin{matrix}CH\cdot C(OH)\\CH:C(OH)\end{matrix}\geqslant N,$$

melting at 254—255°. Ethylic phenylbenzylglutaconate, has been prepared from the product of the interaction of ethylic benzylmalonate and ethylic phenylpropiolate; on treatment with ammonia, it yields *γ-phenyl-β-benzyl-αα'-dihydroxypyridine* melting at 175°.

The author, further, gives an account of some experiments undertaken with the view of examining the action of ammonia on ethylic salts of saturated polycarboxylic acids. Ethylic propanetetracarboxylate is transformed into the diamido-imide of the acid (Ruhemann and Cunnington, *Trans.*, 1898, lxxiii., 1006), but its homologue, ethylic-β-methylpropanetetracarboxylate, forms the tetramide. Ethylic propanepentacarboxylate yields the triamido-imide of the acid,—

$$NH\begin{matrix}CO-CH-CONH_2\\ \quad\quad|\\CO-CH-CH(CONH_2)_2\end{matrix},$$

melting at 212°, but ethylic phenylpropanetricarboxylate is transformed into the triamide melting at 230° with evolution of gas.

The author has also examined the action of sodium ethoxide on a mixture of ethylic phenylpropiolate with ethylic acetoacetate on the one hand, and with ethylic benzoylacetate on the other, and shows that the α-pyrone compounds, represented by the formulæ I. and II. are formed respectively.

$$CO_2Et\cdot C\leqslant\begin{matrix}CPh:CH\\CMe-O\end{matrix}\geqslant CO \qquad CO_2E\cdot C\leqslant\begin{matrix}CPh:CH\\CPh-O\end{matrix}\geqslant CO$$

I. M.-p. 104°. II. M.-p. 120—121°.

The action of ammonia on the first of these compounds has been studied; it does not lead to the formation of a pyridine derivative, but yields the ammonium salt, $NH_2\cdot CMe:C(CO_2Et)\cdot CPh:CH\cdot CO_2NH_4$, which regenerates the pyrone compound on treatment with acids.

8. "*The Changes of Volume due to Dilution of Aqueous Solutions.*" By E. D. H. Wade, B.A.

In this paper, the contraction of solutions of different substances at various concentrations has been studied experimentally. Contraction is defined as the diminution of volume on mixing equal volumes of water and solution, stated for 100,000 c.c. of resulting solution; *e.g.*, if 50 c.c. of water + 50 c.c. of solution yield 99·999 c.c. of diluted solution, the contraction is said to be unity. Concentration is defined as the number of grm.-equivalents of substance in every 100,000 c.c. of the solution after dilution.

The author describes an apparatus for measuring such contractions directly to within about one-tenth of a unit without the need of determining the specific gravities of the experimental liquids. Observations were made on solutions of hydrogen, sodium, potassium, calcium, and strontium chlorides, potassium ferrocyanide, oxalic acid, cane-sugar, and urea. In almost all cases the equation—

$$X = \frac{n^b}{a}$$

was found to hold good in which X is contraction, n concentration, and a b are constant terms. In such cases, ϕ, the apparent volume of the substance, must be given by—

$$\phi = \text{const.} + \frac{n^b - 1}{a(2^b - 1)},$$

and values of ϕ thus calculated for various values of n are tabulated in the paper.

The first equation shows how X varies with the concentration. If the concentration be kept constant, and the dissolved substance varied, it is found that X increases regularly with the equivalent weight of the dissolved substance.

The apparatus described is available for many other cases where a change of volume follows a chemical process, as in the neutralisation of an acid.

9. "*The Thermal Effects of Dilution.*" By J. Holms Pollok, B.Sc.

In thermo chemical determinations it is customary to operate with very dilute solutions to simplify the calculations connected therewith. To determine how far dilution might affect the thermal condition of salts in solution, a number of saturated solutions of salts were diluted with an equal bulk of water, and the following changes of temperature were noted:—

Saturated solutions at 9°.	Thermal change on dilution. 1st expt.	2nd expt.
NaCl	+0·50	+0·50
$NaNO_3$	−1·80	−1·85
Na_2SO_4	−0·05	−0·03
Na_2CO_3	−0·15	−0·20
KCl	−0·47	−0·47
KNO_3	−0·32	−0·38
K_2SO_4	−0·04	−0·03
K_2CO_3	−0·37	−0·44
NH_4Cl	−0·15	−0·13
$(NH_4)_2SO_4$	−0·43	−0·39
$CaCl_2$	+0·58	+0·62
$BaCl_2$	−0·07	−0·06
$MgSO_4$	+0·02	−0·01
$ZnSO_4$	+0·03	+0·05
$CuSO_4$	+0·02	+0·05
$FeSO_4$	+0·04	+0·00
$Pb(NO_3)_2$	−0·37	−0·33

The method employed was as follows:—Saturated solutions of the various salts were made, and half a litre of each placed in glass bottles of that capacity; an equal number of bottles were filled with half a litre each of distilled water, then all were placed in a large, shallow, wooden tub, in a room of uniform temperature, and left for twenty-four hours. A number of thin glass beakers of about a litre capacity, with glass stirring-rods shaped into a ring at the end, were provided, also a mercury thermometer graduated into tenths of a degree, and reading easily to a quarter of each division, as well as a differential alcohol thermometer with only about 4° on the whole stem, and the graduations of which corresponded to less than 0·01°. The temperatures of the bottles were taken as the experiments were made, and were found to be almost exactly 9°, though the different bottles did in point of fact vary as much as 0·05°, for which a proper correction was made. A bottle of solution and a bottle of water were then lifted out of the bath by a piece of flannel and poured simultaneously into a beaker standing on a thick piece of flannel, stirred up, and the temperature noted by both thermometers.

10. "*Halogen Derivatives of Acetonedicarboxylic Acid.*" Part I. By Frederick W. Dootson, M.A.

This communication is a preliminary note of an investigation of the action of halogens on ethylic acetonedicarboxylate. By the action of dry chlorine, *ethylic tetrachloracetonedicarboxylate* has been obtained. This substance, after purification, is a colourless, crystalline compound which melts at 30—30·5°, and decomposes on hydrolysis with aqueous soda or potash. It reacts with alcoholic potash, forming dichloromalonic and dichloracetic acids, and with ammonia yielding the amides of these acids. The action of bromine is very similar to that of chlorine.

11. "*The Detection and Determination of Sucrose in the presence of Lactose.*" By Edwin Dowzard.

The method proposed by the author is based on the

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fact that sucrose is inverted by citric acid, whilst lactose is unaffected. The rotatory power of a solution of lactose is determined before and after treatment with citric acid. If the lactose is pure the rotation remains unchanged, but if sucrose is present it is considerably decreased. The amount of sucrose is readily calculated from the decrease in rotation.

12. "*Note on the Interaction of Formaldehyde with β-Naphthylamine Derivatives.*" By G. T. Morgan, B.Sc.

With a view of explaining the interactions which occur between formaldehyde and β naphthylamine (*Trans.*, 1898, lxxiii., 536), the author has investigated the action of this reagent on alkyl, benzyl, and halogen derivatives of the base.

Dibenzyl β-naphthylamine, $C_{10}H_7N(CH_2Ph)_2$, crystallises from alcohol in colourless leaflets, and from ethylic acetate in clusters of hard transparent prisms; it melts at 119—120°.

One compound only results when formaldehyde reacts with dialkyl- and dibenzyl β-naphthylamine, two molecular proportions of the base condensing with one of the aldehyde to form a dinaphthylmethane derivative. The following compounds have been obtained: *tetramethyl-ββ-diaminodinaphthylmethane*, $CH_2(C_{10}H_6NMe_2)_2$, which crystallises in transparent colourless prisms melting at 144°, the *tetrethyl* derivative, $CH_2(C_{10}H_6NEt_2)_2$, which crystallises in large colourless prisms and melts at 114°, and the *tetrabenzyl* derivative, $CH_2[C_{10}H_6N\cdot(CH_2Ph)_2]_2$, which forms lustrous leaflets melting at 164°.

The formation of these derivatives seems to be due to substitution in the contiguous α-position, as compounds of a different type are formed with methylene in the side chain when a halogen atom occupies this α-position.

Methylene 1-bromo-2-naphthylamine, $C_{10}H_6BrN{:}CH_2$, is obtained when 1-bromo-2-naphthylamine is treated with formaldehyde in acetic acid or in alcoholic solution; it crystallises from benzene or chloroform in colourless needles, and melts, with decomposition, at 144—145°. The corresponding *chloro*-derivative, $C_{10}H_6Cl\cdot N{:}CH_2$, obtained from 1-chloro-2-naphthylamine crystallises in colourless needles and melts at 179—180°. Both substances are compounds of the anhydroform-aldehyde type, and are converted into their generators on hydrolysis with acids, whilst the dinaphthylmethane bases are not altered under these conditions.

The investigation is being extended to other derivatives of β-naphthylamine.

PHYSICAL SOCIETY.

Ordinary Meeting, January 27th, 1899.

Mr. G. Griffith, M.A., Vice-President, in the Chair.

A mathematical paper was read by Dr. E. H. Barton, on "*The Equivalent Resistance and Inductance of a Wire to an Oscillatory Discharge.*"

Maxwell's treatment of the self-induction of cylindrical conductors was extended by Lord Rayleigh, in an article published in the *Phil. Mag.* for May, 1886, to alternate currents that follow the harmonic law at constant amplitude. Dr. Barton now modifies the analysis, and further extends it to include the decaying periodic currents obtained in discharging a condenser, and to the case of damped trains of high frequency, *i.e.*, to Hertz waves in general. The theoretical value (R″/R′) for the ratio of equivalent resistances to waves, respectively with and without damping, agrees very well with Dr. Barton's experimental results.

Mr. Oliver Heaviside, in a communication (here abstracted) said that he had, by another method of mathematical analysis, arrived at the same value as Dr. Barton for (R″/R′). In addition to the causes hitherto suggested as affecting the attenuation factor, it was possible that the conductivity of the wires to vibrations millions per second might be less than with steady currents, and that the voltage at the beginning of the wave-train might be large enough to cause some leakage. Both resistance and inductance become infinite with infinite damping, and they differ somewhat from the corresponding quantities for undamped waves.

Mr. Rollo Appleyard then described (1) some Experiments upon Dephlegmators, in which he has attempted to replace the platinum-gauze valves of the ordinary fractionating-tubes by bends in the tubes. The general form of the apparatus consists in a series of elongated bulbs, the top of each being connected to the bottom of the one above it by a horizontal S-shaped tube. The vapour condensed in any intermediate bulb falls back into the preceding S-bend. The first portions of the distillate are thus returned to the boiling-flask, leaving a little at each bend to act as a wash for the ascending vapour. At the early stage of distillation the bulbs and bends behave as required, but it is found that at the later stages certain of the bulbs become completely filled with liquid sustained by the upward pressure of the vapour, and, unless the heating is very carefully managed, "geyser" actions may take place. Some arrangement of overflow tubes is therefore required for the bulbs.

Mr. Appleyard also exhibited (2) a Temperature Tell-tale, to be used in connection with vats, and for other purposes where an alarm is to be sounded by making electric contact when temperature rises or falls beyond certain limits. A J-shaped glass tube has its short limb sealed and its long limb open. Water or other suitable liquid is poured in, completely filling the short limb. Mercury is then made to displace nearly all the water in the short limb; the surplus water in the long limb is removed by a pipette, and the mercury is adjusted to a convenient level. Two platinum contact-wires are sealed into the glass at a short distance above the free surface of mercury in the long limb. The tube may be half an inch in diameter, with a long limb of 5 inches and a short limb of 2½ inches. The quantity of mercury in the tube is generally arranged so that, at temperatures below the boiling-point of the contained liquid, the mercury level is lowest in the long limb. In this case, if the temperature is raised to the boiling-point of the contained liquid, the mercury assumes approximately a common level in both limbs, for at the boiling-point of the liquid, under these conditions, the vapour-pressure is equal to the barometric pressure. Hence the liquid and the mercury are not spurted out.

Mr. Whopple said that when working with an ordinary "thermometer" tube the contacts were inefficient, owing to oxidation. Moreover, the mercury column broke up, and in some cases mercury clung to the contact-wire. He asked if these difficulties occurred in Mr. Appleyard's apparatus.

Mr. Watson suggested that in some cases the long limb might with advantage be closed. With regard to the dephlegmator he thought that the bends should each be duplicated by a short tube, so as to provide one path for the descending liquid and another for the ascending vapours. This seemed to be the object of the platinum gauze in fractionating-tubes.

Mr. Appleyard, in reply, explained that the change of level in the "tell-tale" was a sudden rise of about an inch of mercury, in a tube about half an inch in diameter. This rise was able completely to envelope the contact-wires, surface oxidation could not affect the working, and there could be no such thing as failure of contact. Moreover, the tube was too wide for mercury to be held up by capillarity. The large area of contact enabled the instrument to be used for strong currents. The cost was small, and the only adjustment consisted in choosing a liquid of suitable boiling-point, for the platinum wires could be sealed in anywhere in the long limb—about 2½ inches from the bottom was a good position for them. The sudden rise occurred when the temperature was one or two degrees above the boiling-point of the contained liquid.

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Mr. T. H. Littlewood then read a paper on "*The Volume-changes which accompany Solution*," and described an apparatus for measuring the contraction observed when solids are dissolved in a liquid.

Two glass bulbs are arranged one above the other, so that liquid can pass from the upper one to the lower one through a stopcock, and from the lower one upwards into the neck of the upper one through a second stopcock. This neck, which forms the top of the upper bulb, is fitted with an indiarubber stopper. The lower bulb is tubulured and provided with a glass stopper. A horizontal capillary tube is fitted into the indiarubber stopper, so that volume-changes can be determined, after the manner of using Bunsen's calorimeter. The weighed solid is introduced at the tubulure. The measured amount of water is poured in at the neck. Paraffin oil is now poured in at the tubulure, so that the apparatus is completely filled—the lower bulb with the solid and the oil, the upper bulb with the water. The apparatus is then exhausted, and finally it is placed in a tank of water at constant temperature. When the stopcock between the bulbs is opened, solution begins, and the resulting contraction is measured. For small amounts of salt dissolved in constant volume of liquid, the contraction is very nearly proportional to the amount of salt. For larger amounts, the contraction is greater in proportion than the added salt. If a strong solution is gradually diluted, then, for equal amounts of water added, the contraction becomes smaller for successive amounts of added water. Mr. Littlewood applies Ostwald's theory, and the theory of Van der Waals to the observed results, and expresses the contraction as a logarithmic function of the volumes and the internal pressures.

Mr. Lehfeldt thought the indiarubber stopper was a weak point in the apparatus. With regard to the theory of the contraction, Tammann (*Zeitsch. fur Phys. u. Chem.*, 1895) had given an expression which was rather more intelligible. Tammann found that the effect could be regarded as equivalent to a change of pressure, and, by attributing this quality to the solution, the characteristic surface becomes the same as that for water. The volume of the solution would thus follow similar changes to those that water undergoes with increasing pressures.

Prof. Ewing said the experiments reminded him of the very first piece of research work he had done in physics, which was twenty-five years ago, on the same problem, with Mr. McGregor. An examination of the electrical properties of solutions of certain salts led to an investigation of their changes of density and volume. In some cases the contraction observed was so great that the volume of the solution was less than the original volume of the water to which the salt had been added. They made some measurements, but the apparatus they had used was very rough compared to that described by Mr. Littlewood.

Mr. Watson asked whether Mr. Littlewood had made any simultaneous density measurements. There were some solutions for which the contractions and corresponding densities had been worked out. By examining successive dilutions of strong solutions, and the corresponding densities, a check might be made as to the numerical results obtained by Mr. Littlewood's apparatus.

Dr. Chree suggested that, in place of the logarithmic expression, the total contraction might possibly be better represented by a few terms of a series involving increasing powers of the difference of volume, each term being multiplied by a proper constant.

Mr. Littlewood, in reply, said that the indiarubber stopper possessed advantages in regulating the height of the capillary tube. It did not introduce sensible error, for it was possible to work with it to a centigrm. of mercury in the capillary. On the other hand, temperature-changes of one-tenth of a degree involved 1 centigrm. more or less of mercury in the tube. Bunsen, using an indiarubber stopper, obtained very accurate results in calorimetry.

The Chairman proposed votes of thanks, and the meeting adjourned until February 10th (Annual General Meeting).

CORRESPONDENCE.

THE ESTIMATION OF MANGANESE BY MEANS OF POTASSIUM PERMANGANATE.

To the Editor of the Chemical News.

In his letter of last week Mr. Brearley asks for my opinion on the fact that a permanganate solution standardised by means of iron gives low results when manganese is being estimated.

Everyone who has tried to standardise bichromate by means of iron wire dissolved in dilute hydrochloric, and more so in sulphuric acid, knows the effect of the traces of carbon present on the "finish." This well-known source of error in the case of bichromate or permanganate I always remove, so that the low results I have obtained cannot be accounted for in that way.

The obvious explanation of course is that the usually accepted equation for the action of permanganate on manganous sulphate does not, in the circumstances under discussion, quite represent the reaction taking place. This is not such an unusual occurrence that it need be classed as anomalous.

In regard to the ignition of Mn_3O_4 in a platinum crucible, Mr. Brearley goes rather astray when he points out that the products of combustion may have a prejudicial effect, as Gooch and Austen (*Am. Journ. Sci.*, 1898, v., 209-214) point out that this is beneficial rather than otherwise.—I am, &c.,

F. W. Daw.

ESTIMATION OF LEAD.

To the Editor of the Chemical News.

Sir,—I have to thank Mr. R. Leffler for his letter *re* "Estimation of Lead."

I had previously tried the molybdate method and found it to work very satisfactory on ores, in which case I evaporated the solution of the ore in a basin with sulphuric acid to near dryness, diluted with water, filtered and treated residue with an acetate, which was then immediately titrated with molybdate, using tannin as indicator.

But in the estimation of such small quantities of lead in slags, with so much iron present, this method is not satisfactory owing to the difficulty of washing the sulphate residue free of iron, which if left in makes the end reaction.

The bichromate method I find excellent if sufficient time is allowed, but which, unfortunately, is not the case.—I am, &c.,

Cox.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

Note.—All degrees of temperature are Centigrade unless otherwise expressed.

Comptes Rendus Hebdomadaires des Séances, de l'Académie des Sciences. Vol. cxxvii., No. 25, December 19, 1898.

This number contains a report of the Annual Public Meeting of December 19th.

The Jecker Prize in Chemistry was divided between MM. G. Bertrand, Buisine, and Daniel Berthelot.

M. Bertrand first worked for some time on the crystalline compounds which give zinc hydrate with the metals

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of the alkaline earths. About the same time he identified the colouring matter of pollen with carotene. Since these early researches, he undertook the investigation of lignous tissue, which he found to be essentially different in angiosperms and gymnosperms. During this research he prepared considerable quantities of a sugar, xylose, which was very rare at that time. Xylonobromide of cadmium followed from this; and later, in conjunction with Emile Fischer, M. Bertrand synthesised lixose. His last work was an exhaustive examination of ferments, during which he discovered a new group of these substances, which he called *oxydases*.

Alphonse Buisine began his series of researches by finding, in collaboration with Ed. Duviller, the conditions under which the mono-, di-, and tri-amines of the fatty series are formed, and the methods of separating these amines. His next work was the investigation of the chemical composition of mutton fat. He has also published a method which permits of the preparation of ferric sulphate, ferrous sulphate, and ferric chloride from the residue of pyrites roasting.

Daniel Berthelot in his first published work proposed to apply the method of electrical conductivities to the general investigation of the neutralisation of the principal organic acids, the chief aim being to examine the formation of the neutral salts, acids, and bases produced by the monobasic and polybasic acids, the dissociation under the influence of excess of water, base or acid, and finally, the influence which the different functions exert when joined to the acid function. He has arrived at very interesting results, obtained by the method of conductivities, which agree in the main with those given by thermochemical methods. He has found new methods of investigating the basicity of acids, their functions, and their isomers. Besides these, M. Berthelot has published researches on "The Measurement of Temperature," "Fusion-points of Silver and Gold," "The Determination of Molecular Weights of Gases from their Densities and the Divergence which they show from Marriotte's Law," "Laws of Gaseous Mixtures."

Bulletin de la Société Chimique de Paris.
Series 3, Vol. xix.-xx., No. 11.

Remarks on the Principle of Maximum Work.—D. Tommasi.—The author deduces as the result of his researches, that when a body is submitted to two chemical actions, the reaction which gives off the most heat will always take place by preference if it can be started; and that between two chemical reactions the one which requires the least heat or energy will always take place first, even if it gives off less heat than the other one.

Atomic Refraction of Metals in the Metallic Carbonyls, and the Constitutional Formulæ of these Derivatives.—A. J. Ferreira da Silva.—A controversial paper relating to some remarks by M. Nasini on a previous communication by the author.

Action of Chlorine on Chloride of Ethylene in the yresence of Chloride of Aluminium.—A. Mouneyrat.—250 grms. of perfectly dry chloride of ethylene, $CH_2Cl—CH_2Cl$, was placed with 25 grms. of chloride of aluminium in a perfectly dry flask of 250 c.c. capacity fitted with a vertical condenser. On heating to 80—85°, an abundant disengagement of hydrochloric gas takes place. If this gas is passed through weak potash, to remove the hydrochloric acid, a gas still comes over which is unabsorbed by the potash and can be collected in test-tubes under water; it burns, leaving a deposit of carbon, and if passed into a tube wetted with ammoniacal cuprous chloride a red precipitate is obtained. This gas belongs to the group of acetylenic carbides. It is completely absorbed by bromine, which, when treated with potash, gives a colourless oily liquid, heavier than water, with the formula $C_2H_2Br_4$; that is to say, tetrabromide of acetylene. If the preceding mixture is passed into dry chlorine, this body should combine with the acetylene as soon as it is formed. The colourless liquid obtained is submitted to fractional distillation. Between 84—90° a large quantity of liquid comes over; then the thermometer rises to 130°, and the remainder comes over at 130—150°. The first portion is unattacked chloride of ethylene, and from the other we obtain two liquids, one boiling at 130—136°, and the other at 145—147°. The first contains 84 per cent of chlorine, and is the dissymmetric tetrachloride of carbon, $CH_2Cl—CH_2Cl_3$; the second one also contains 84 per cent of chlorine, and is a symmetrical tetrachloracetylene, $CHCl_2—CHCl_2$.

Chlorisation of Acetylene.—A. Mouneyrat.—In the chlorisation of $CH_2Cl—CH_2Cl$ in the presence of $AlCl_3$, the author has never had an explosion, though in the ordinary way chlorine mixed with acetylene always explodes, and from this fact he thought that by increasing the amount of acetylene in the previous experiment, the return of $CHCl_2—CHCl_2$ might be augmented. Experiment proved this to be the case. Further experiments showed that it was the absence of free oxygen, and of any gas capable of furnishing it, which prevented any explosion.

Preparation of Tetrachloride of Acetylene.—A. Mouneyrat.—In the foregoing experiments the author has shown that explosions are prevented during the preparation of tetrachloride of acetylene by rigidly excluding the air. He now describes a more perfect form of apparatus in which this operation can be carried on, producing as much as 1 kilogrm. in twenty-four hours. It is also pointed out that the chloride of ethylene can be replaced by tetrachloride of carbon, CCl_4, and the $AlCl_3$ suppressed, though the former method is the better one.

Action of Chlorine on Tetrachloride of Acetylene, $CHCl_2—CHCl_2$, in the presence of Chloride of Aluminium. Preparation of Hexachlorethane (C_2Cl_6).—A. Mouneyrat.—The chloridising power of chloride of aluminium does not depend on the quantity of this body added to the substance to be chloridised, but it is simply a function of the temperature. 250 grms. of tetrachloride of acetylene and 30 grms. of anhydrous chloride of aluminium were placed in a flask as before, and heated in a paraffin bath, and a current of dry chlorine passed through. If kept at 100° for four or five hours only small quantities of hexachlorethane are formed, but if the temperature is raised to 118—120° the action becomes very rapid. The flask soon becomes full of a white substance smelling very strongly of camphor. This is thrown into dilute hydrochloric acid to remove the chloride of aluminium; it is then washed with distilled water, thoroughly dried, and purified by sublimation. It melts in a capillary tube at 187—188°, and contains 89·5 per cent of chlorine. Theoretically, C_2Cl_6 contains 89·8 per cent of chlorine; this body is therefore hexachlorethane.

Constitution of Camphoric Acid and of Camphor.—L. Bouveault.—A very long paper, not suitable for abstraction.

Analysis of Muds Precipitated during the Electrolytic Refinement of Copper.—A. Hollard.—These muds are found to contain gold, silver, salts of arsenic, antimony, lead, bismuth, copper, selenium, and tellurium. They are valuable on account of the large quantities of gold, silver, and copper they contain.

Estimation of Formic Acid in the presence of Acetic Acid and of Easily Oxidisable Organic Bodies.—A. Leys.—Already inserted in full.

Detection of Sawdust in Bread.—G. A. Le Roy.—This falsification is detected by coloured reactions produced on the celluloses by orcine, amidol, indol, pyrrol, &c.

New Suction Pump.—MM. Bourcet and Berlemont.—This cannot be explained without the accompanying diagram.

The Chloridising Action of Ferric Chloride in the Aromatic Series.—V. Thomas.—Already inserted.

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MEETINGS FOR THE WEEK.

MONDAY, 6th.—Society of Arts, 8 (Cantor Lectures). "Bacterial Purification of Sewage," by Dr. Samuel Rideal.
TUESDAY, 7th.—Royal Institution, 3. "The Morphology of the Mollusca," by Prof. E. Ray Lankester, M.A., LL.D.
WEDNESDAY, 8th.—Society of Arts, 8. "Nernst's Electric Lamp," by James Swinburne.
THURSDAY, 9th.—Royal Institution, 3. "Toxins and Antitoxins," by Dr. Allan Macfadyen, M.R.C.S.
—— Society of Arts, 8. "The Penal System at the Andamans," by Colonel Richard Carnac Temple, C.I.E.
FRIDAY, 10th.—Royal Institution, 9. "The Motion of a Perfect Liquid," by Prof. H. S. Hele-Shaw, LL.D.
—— Physical, 5. (Annual General Meeting). Address by the President. "An Ampère-Meter and a Volt-Meter with a Long Scale," by Benjamin Davies.
SATURDAY, 11th.—Royal Institution, 3. "The Mechanical Properties of Bodies," by The Right Hon. Lord Rayleigh, F.R.S., &c.

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THE CHEMICAL NEWS.

VOL. LXXIX., No. 2046.

ON THE BOILING-POINT OF LIQUID HYDROGEN UNDER REDUCED PRESSURE.*

By JAMES DEWAR, M.A., LL.D., F.R.S.

THE June number of the *Proceedings of the Chemical Society* contains a paper by the author on "The Boiling-point and Density of Liquid Hydrogen." A resistance thermometer made of fine platinum wire, called No. 7 Thermometer, was used in the investigation. It had been carefully calibrated, and gave the following resistances at different temperatures:—

Temperature. °C.	Resistance. Ohms.
+99·1	7·337
+75·3	6·859
+51·4	6·388
+25·7	5·857
+0·7	5·338
−78·2	3·687
−182·6	1·398
−193·9	1·136
−214·0	0·690

The zero of the thermometer in platinum degrees was −263·27°. Mr. J. D. Hamilton Dixon, M.A., Fellow of Peterhouse, who contributed a paper to the *Phil. Mag.* for June, 1898, on "The Reduction of Normal Air Temperature of the Platinum Thermometers," used in the low temperature researches of Professor Fleming and the author, has been good enough to calculate a special formula for this thermometer No. 7. He finds the formula—

$$(R + 43{\cdot}958933)^8 = 2{\cdot}03596488\ (t + 1193{\cdot}1460)$$

expresses the relation between the resistance and temperature in centigrade degrees. This expression gives a probable error of only 0·16° C. over a range of more than 300° C. When this thermometer was placed in boiling hydrogen, the resistance became 0·129 ohm, and remained constant at this value. Calculated into the Dickson formula, this value of the resistance corresponds to a temperature of −238·4° C. If we assume the resistance reduced to zero, then the temperature registered by the thermometer ought to be −244° C. At the boiling-point of hydrogen, therefore, if the law correlating resistance and temperature can be pressed to its limits, a lowering of the boiling-point of hydrogen by 5° or 6° C. would produce a condition of affairs where the platinum would have no resistance, or become a perfect conductor. Now we have every reason to believe that hydrogen, like other liquids, will boil at a lower temperature the lower the pressure under which it is volatilised. The question arises, How much lowering of temperature can we practically anticipate? For this purpose we have the boiling-point and critical data available from which we can calculate an approximate vapour-pressure formula, accepting 35° abs. as the boiling-point, 52° abs. as the critical temperature, and 19·4 At. as the critical pressure; then as a first approximation—

$$\log p = 6{\cdot}8218 - \frac{137{\cdot}9}{T}\ \text{m.m.} \quad . \quad . \quad . \quad 1.$$

If instead of using the critical pressure in the calculation, we assume the molecular latent heat of hydrogen is proportional to the absolute boiling-point, then from a comparison with an expression of the same kind, which gives accurate results for oxygen temperatures below one atmosphere, we can derive another expression for hydrogen vapour-pressures, which ought to be applicable to boiling-points under reduced pressure.

The resulting formula is—

$$\log p = 7{\cdot}2428 - \frac{152{\cdot}7}{T}\ \text{m.m.} \quad . \quad . \quad . \quad 2.$$

Now Formula 1 gives a boiling-point of 25·4° Ats. under a pressure of 25 m.m., whereas the second equation (2) gives for the same pressure 26·1° Ats. As the absolute boiling-point under atmospheric pressure is 35°, both expressions lead to the conclusion that ebullition under 25 m.m. pressure ought to reduce the boiling-point some 10° C. For some time experiments have been in progress with the object of determining the temperature of hydrogen boiling under about 25 m.m. pressure, but the difficulties encountered have been so great, and repeated failures so exasperating, that a record of the results so far reached becomes advisable. The troubles arise from the conduction of heat by the leads; the small latent heat of hydrogen volume for volume as compared with liquid air; the inefficiency of heat isolation and the strain on the thermometer brought about by solid air freezing on it and distorting the coil of wire. In many experiments the result has been that all the liquid hydrogen has evaporated before the pressure was reduced to 25 m.m., or the thermometer was left imperfectly covered. The apparatus employed will be understood from Fig. 1.

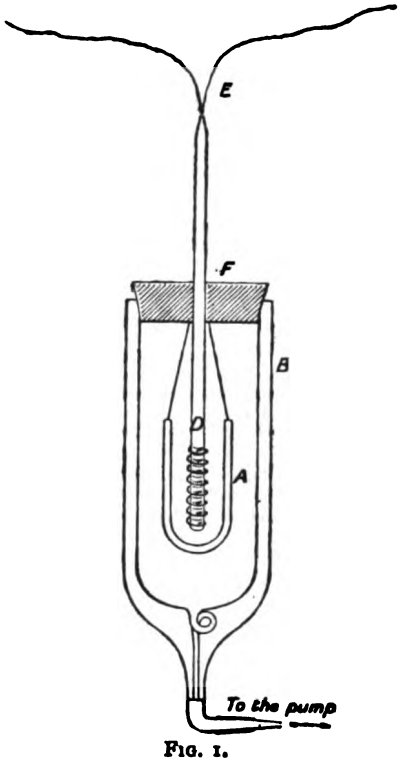

FIG. 1.

The liquid hydrogen collected in the vacuum vessel A was suspended in a larger vessel of the same kind B, which is so constructed that a spiral tube joins the inner and outer test-tubes of which B is made, thereby making an opening into the interior at C. The resistance thermometer D and leads E pass through a rubber cork F, and the exhaustion takes place through C. In this way the cold vapours are

* A Paper read before the Royal Society, December 15, 1898.

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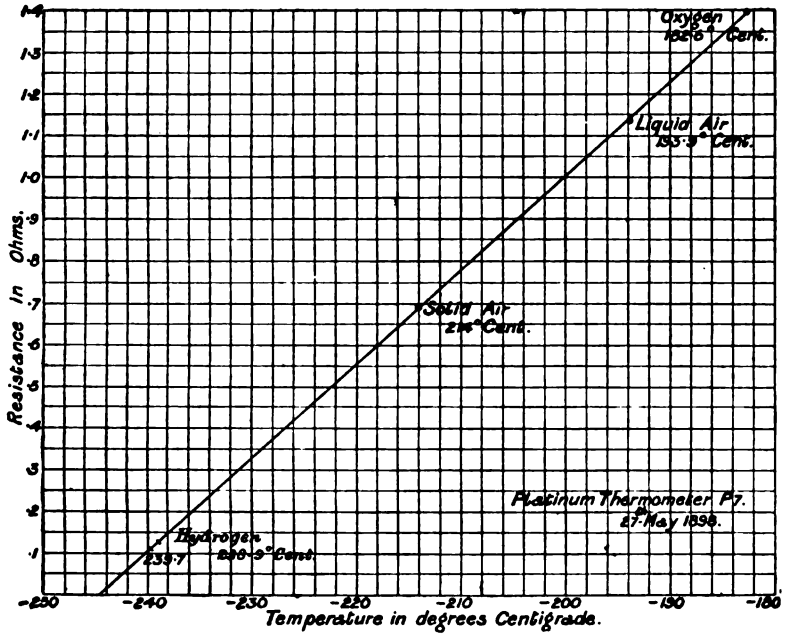

FIG. 2.

drawn over the outside of the hydrogen vacuum vessel, and this helps to isolate the liquid from the connective currents of gas. To effect proper isolation, the whole apparatus ought to have been immersed in liquid air under exhaustion. Arrangements of this kind add to the complication, so in the first instance the liquid was used as described. The liquid hydrogen evaporated quietly and steadily under a pressure of about 25 m.m. of mercury without the least appearance of solidification or loss of mobility; still remaining clear and colourless to the eye. Naturally the liquid does not last long, so the resistance has to be taken quickly. Just before the reduction of pressure began, the resistance of the thermometer was 0·131 ohm. This result compares favourably with the former observation on the boiling-point, which gave a resistance of 0·129 ohm. On reducing the pressure, the resistance diminished to 0·114 ohm, and kept steady for some time. The lowest reading of resistance was 0·112 ohm. This value corresponds to −239·1° C., or only one degree lower than the boiling-point at atmospheric pressure, whereas the temperature ought to have been reduced some 10° C. or in any case 5° under the assumed exhaustion. The position of the observation on the curve of the relation of temperature and resistance for No. 7 thermometer is shown on the diagram (Fig. 2). The question arises then as to what is the explanation of this result? Has the platinum resistance thermometer arrived at a limiting resistance about 35° Abs., so that at a lower temperature it refuses to change in resistance, the curve having become practically asymptotic to the axis of temperature? On the other hand, has the influx of heat by the leads, and the correction on account of this change of resistance become so great as to vitiate the results at these excessively low temperatures? Again, it may be suggested that the thermometer was not properly cooled, or that the liquid hydrogen does not lower in temperature to any marked extent under exhaustion like other liquids. All these conjectures can only be set at rest by a repetition of the experiments with a new thermometer of much higher initial resistance, and under conditions of better heat isolation. No blunder having been detected in the observations, for the present we must assume that the platinum resistance thermometer No. 7 acts in the manner described. It would be premature to discuss the inferences to be drawn from these results until they are confirmed on another variety of platinum wire made into a resistance thermometer. But as this will involve the use of considerable quantities of liquid hydrogen, it will take some time to complete the investigation.

The same kind of anomaly appears in the case of the use of a thermojunction at these low temperatures, but this is a separate matter, and must be dealt with in a further communication.

I am indebted to Mr. J. E. Petavel for assistance in the electrical measurements, and also to Mr. Robert Lennox and Mr. Heath for their general help in the conduct of the experiments.

THE CONSTITUTION OF THE ELECTRIC SPARK.*

By ARTHUR SCHUSTER, F.R.S., and G. HEMSALECH.

WHEN an electric spark passes between metallic electrodes, the spectrum of the metal appears, not only in immediate contact with the electrodes, but stretches often across from pole to pole. It follows that during the short time of the duration of the spark the metal vapours must be able to diffuse through measurable distances.

The following investigation was undertaken primarily to measure this velocity of diffusion with the special view of comparing different metals, and different lines of the same metal.

Feddersen published, in the year 1862, an interesting research, in which photographs of sparks passing between different metal poles are taken after reflection from a rotating mirror. He could from his experiments draw some conclusions which have a bearing on our subject, but it was necessary for our purpose that the light should also be sent through a spectroscope, so as to distinguish

* Abstract of a Paper read before the Royal Society, February 2, 1899.

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between the luminous particles of air and those of the metal poles.

The method of the rotating mirror tried during the course of several years in various forms by one of us did not prove successful. On the other hand, good results were obtained at once on trying the method used by Professor Dixon in his researches on explosive waves. This method consists in fixing a photographic film round the rim of a rotating wheel. All that is necessary for its success is to have sparks so powerful that each single one gives a good impression of its spectrum on the film. Were the sparks absolutely instantaneous, the images taken on the rotating wheel would be identical with those developed on a stationary plate, but on trial this is found not to be the case. The metal lines are found to be inclined and curved when the wheel rotates, and their inclination serves to measure the rate of diffusion of the metallic particles. The air lines, on the other hand, remain straight, though slightly widened.

To avoid the tendency of the film to fly off the wheel when fixed round its rim, as in the original form of the apparatus, a spinning disc was constructed for us by the Cambridge Scientific Instrument Company. The film is placed flat against the disc, and is kept in place by a second smaller disc, which can be screwed lightly to the first. The diameters of the two discs are 33 and 22·2 c.m., the photographs being taken in the annular space of 10·8 c.m., left uncovered by the smaller disc. An electric motor drives the disc, and we have obtained velocities of 170 turns per second, though in our experiments the number of revolutions was generally about 120, giving a linear velocity of about 100 metres/second for that part of the film on which the photograph was taken.

The electric discharges were obtained from a battery of six Leyden jars, having a total capacity of 0·033 microfarad, and being charged from an induction machine constructed for us by Mr. H. C. Wimshurst. This machine has twelve plates of 62 c.m. diameter, and give sparks which are 13 inches long.

The electrodes were, as a rule, placed 1 c.m. apart, and an image of the spark was projected on the slit of the spectroscope, the distance of the slit from the electrodes being equal to four times the focal length of the projecting lens, so that the image was equal in size to the spark. The prism used was made by Steinheil, and had a refracting angle of 60°.

We may now pass to the description of the results obtained when the spectrum of a single spark is taken on a moving film. A preliminary trial with various metallic electrodes had shown us that the sharpest results were obtained with zinc, and we therefore chose that metal for our first investigation. The principal lines of zinc as they appear on our photographs are the double line, the least refrangible of the two having a wave-length 4924·8, and the blue triplet, the wave-length of the leading line being 4810·7. All the lines are curved on the photographs taken with the spinning disc, but the displacements, especially near the poles, are subject to considerable variations. This is probably due to the fact that the path of the metallic particles is not always straight, and, if straight, its image does not necessarily coincide with the slit. A very slight error in measurement will also affect the results considerably when the total displacement measured is small. Our results do not for this reason allow us at present to give any opinion as to the maximum velocity of the particles near the pole; but if these are considerable, they drop down very quickly to speeds which, in the case of zinc, are not far off 500 metres/second.

We have adopted two methods of comparison between different photographs. We have in the first place measured the displacements at a number of nearly equidistant points, and from these measurements we have deduced the time taken for a metallic molecule to pass from the pole to a point 2 m.m. away from it. If this method could be applied in every case it would form a rational and consistent basis of comparison. But the curved lines which are to be measured are often very diffuse near the pole; this, and the continuous spectrum, may render it impossible to obtain satisfactory measurements at that point. In order not to have to reject unnecessarily a large number of measurements because the spectrum near the pole was indistinct, we have adopted another method, which, though less rational than the first, is found to give consistent results. From all our measurements we may deduce certain figures for the molecular velocities at different and generally equidistant points on the photographs, and may take the average of all these figures as the mean velocity of the particle. In the following tables, V_1 will always refer to the mean velocity between the pole and a point 2 m.m. away from it, while V_2 refers to the average velocity taken for different distances, as just explained. The influence of change of capacity and change in the length of the spark was investigated in the case of zinc, and the following tables exhibit the results. As the zinc lines are sharp near the pole, the first of the above methods of measurement could be applied.

TABLE I.—*Average Velocity* (V_1) *in metres/second of Zinc Molecules.*

Sparking distance. C.m.	Wave-length.	Number of jars. 2.	4.	6.
0·51	4925	814	556	416
	4811	1014	668	529
1·03	4925	400	499	415
	4811	501	548	545
1·54	4925	723	1061	435?
	4811	1210	1526	492?

The first striking result to be deduced from the table is the uniformly higher velocity deduced from the double line 4925, as compared with that found when one of the lines of the triplet is measured; for we have ascertained that the two first lines of the triplet are always displaced by the same amount, and the third is so much mixed up with the air lines in its neighbourhood that it cannot be measured. It was one of the objects of the investigation to detect, if possible, differences of this kind, which might be accounted for by the fact that the molecules producing different lines of the same spectrum have not necessarily the same mass. We nevertheless hesitate to ascribe the smaller apparent velocity derived from $\lambda = 4925$ to this reason. This line, as has been mentioned, is one component of a double line, and the doublet is not resolved on the photographs taken with the moving film. Near the pole where the light is strong, the edge of the least refrangible component of the doublet would be considered to be the least refrangible edge of the doublet; but near the centre of the spark the light is weaker, and the lines, owing to the motion of the wheel, are drawn out towards the violet. The most intense portion of the image will here be that part where the two lines are superposed, and in wishing to set the cross wire on the edge of the line, we should be tempted to set it on the edge of the *most* refrangible component. There is reason to believe that this is the cause of the greater deflection of the double line, and the photographs show some signs that if this source of error is eliminated, the molecule giving out the double line moves more quickly than that giving rise to the triplet. We reserve the decision of this point until we have been able to apply greater dispersion.

Comparing the sparks obtained with different capacities, it is found that when the spark gap is small there seems a very curious *diminution* of velocity as the capacity increases; this is not what should have been expected at first sight, as with the large number of jars we should expect higher temperatures, and therefore greater velocity of diffusion. When the spark gap is 1 c.m., the experiments do not reveal any marked change due to capacity. When the gap is increased still further the sparks become very irregular and unsteady, and no certain conclusions can be drawn from our measurements; the numbers

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marked with a query are specially doubtful. When six jars are used practically identical numbers are obtained for all sparking distances, but with small capacity the centimetre spark seems to give a lower result than in the two other cases. While we should not like at present to consider this as an established result, the table serves to show that the centimetre spark and the highest capacity used gives the most consistent numbers, and our experiments with other metals were all made under these conditions, except in the case of bismuth, where clearer spectra were obtained with only two jars.

Comparing different metals with each other, we find in the first place that those having comparatively low atomic weights, viz., aluminium and magnesium, have higher molecular velocities. With magnesium the metal vapour is scattered about to such an extent that no measurements could be made, but the average velocity of the aluminium molecule was found to be over three times as great as that of zinc, the numbers not laying any claim to accuracy. Comparing zinc and cadmium with each other we obtain almost identical numbers, both for the corresponding doublet and triplets.

Bismuth gave remarkable results. In spite of its high atomic weight some of the lines are but little displaced, indicating an average molecular velocity of 1420 metres/second. For other lines the velocity falls down to that of zinc and cadmium, while one line ($\lambda = 3793$) has a still lower velocity.

We have not obtained satisfactory results with mercury; the best were those in which poles used were of zinc or cadmium, which were covered with amalgam. Differences in molecular velocities were obtained for different lines, but the result here is not so certain as with bismuth.

There is obviously no simple law connecting these velocities with the atomic weight.

Dr. Feddersen was led through his researches to the conclusion that the metallic particles after being once torn off from the electrodes by the discharge took no further part in it, were thrown irregularly into the space surrounding the electrodes quite independently of the electric current. Although in some cases, and especially with magnesium poles, there is some evidence that this is partly true, we are led to take the following modified view of the matter.

The initial discharge of the jar takes place through the air; it must do so because there is at first no metallic vapour present. The intense heat generated by the electric current volatilises the metal which then begins to diffuse away from the poles; the subsequent oscillations of the discharge take place through the metallic vapours and not through the air. We find confirmation of this view in a striking experiment which is easily repeated. If a coil of wire be inserted in the spark circuit of a Leyden jar, which may be charged either by a Wimshurst machine or an induction coil, the air lines disappear almost completely, the metallic lines alone remaining; the nitrogen line at 3995 is the only one which seems to remain with undiminished vigour. According to our view we should explain the experiment by saying that the coil which adds self-induction lengthens the duration of the discharge, and allows time for the metallic molecules to diffuse properly into the spark gap. A great part of the energy of the current may then do useful work by heating up the metallic molecules instead of those of air. Mr. Hemsalech is at present engaged in investigating the changes in the metallic spectra which accompany the insertion of self-induction.

The first spark passing through the air will give rise to a sound wave which, during the complete time of the discharge, will only travel a few millimetres. We may therefore consider that the mass of metallic vapours suddenly set free is driven by its own pressure into the partial vacuum formed by the heated air. It would seem more correct to liken the process to that of a gas under pressure flowing into a vacuum than to that of a pure thermal diffusion. There is not much difference between these views, and we may take it that in our experiment we have approximately measured the velocity of sound in the metallic vapours. This gives a relation between their temperature and density. If we neglect the differences in the rates of specific heat we find approximately—

$$V = 80\sqrt{T/\rho},$$

where T is the absolute temperature, and ρ the vapour density referred to hydrogen. Thus for cadmium the average molecular velocity found was 560, and substituting $\rho = 56$ we obtain $T = 2700$, which seems a possible value. Hence we conclude that the molecule of cadmium in the spark cannot have a mass which is much smaller than that directly determined near the boiling-point of the metal.

In conclusion we have also taken some photographs in which the slit was directly focussed on the sensitive film without the interposition of the film. The photographs show a straight image of the slit followed by a number of curved bands extending from both poles into the spark gap.

The straight image we consider to be the initial discharge through air creating sufficient heat to fill the space with vapour through which the oscillating discharges may then pass. Our experiments point to the fact that the periodic time was rather too small in our experiments to give the best results. The metallic molecule before it has had time to reach through a sufficient distance was possibly affected in its motion by the subsequent oscillation. We hope to remedy this defect by introducing still higher capacities than those used. Our experiments allow us to give the following approximate numerical data. The air rendered luminous by the first discharge remains luminous for a time of about 5×10^{-7} seconds, the metallic vapours then begin to diffuse and reach the centre of the spark (the gap being 1 c.m. long) in a time which, in the case of cadmium, was about 6×10^{-6} seconds. The periodic time of the oscillations with our six jars and a circuit possessing as little self-induction as possible was about 2×10^{-6} seconds. The metallic vapours remain luminous in the centre of the spark for a longer period than near the poles, the duration of the time during which some luminosity can be traced with a discharge from six Leyden jars is about $1{\cdot}5 \times 10^{-4}$ seconds.

NOTES ON THE ESTIMATION OF TUNGSTEN.

By HARRY BREARLEY.

In his paper (Chemical News, vol. xxiv., p. 175) on the "Estimation of Molybdic Acid as Plumbic Molybdate," Chatard remarks that "analogy would seem to offer a good method for tungstic acid, and experimental analyses were made for this purpose, but after repeated trials the process was finally abandoned, as the precipitate came down so finely divided that it passed through the filter. The precipitation, however, seems to be complete, and I have hopes that with closer filter paper greater success will be obtained."

Chatard's difficulty of thirty years ago has long since been overcome, both in the matter of filter-papers* which

* The precipitate easily subsides without the addition of alkaline salts, so that until it is actually on the filter there is no difficulty. With pulp filters, which I use wherever possible, the washing is a very tedious operation unless suction is used. In the latter case, and with pulp filters, the suction may be strongly and safely applied, the washing is so agreeably rapid that added alkaline salts are quite dispensable. The suction referred to is not generally applied as usual by means of the filter-pump, but by arranging a flask as usual for pressure filtering and sucking with the mouth by means of a piece of rubber tubing attached to the bent glass tube which passes through the stopper. In this way, with a flask of several hundred c.c. capacity, it is possible to obtain a partial vacuum equal to 12 inches of mercury; and as, using pulp filters, the vacuum is destroyed only by the wash-water passing through the precipitate, one rarefaction can be made to serve for one complete washing. Ordinary rubber tubing closes up under a pressure of 9 to 12 inches of mercury.

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would have filtered his identical sample, and by the addition of ammonium salts, which have been shown to make the precipitate more easily filterable.

The inducement to re-examine the precipitation of tungsten as lead tungstate lay in the fact that the amount of ($PbWO_4$ and $PbMoO_4$) precipitated from a known mixture of tungstic and molybdic acids under such circumstances as had always precipitated molybdic acid alone as true $PbMoO_4$, led to the conclusion that the lead tungstate was not strictly represented by the formula $PbWO_4$, and further that the general analogy which Chatard foresaw did not go very far. When it is remembered that tungsten and molybdenum in a mixture are frequently estimated by precipitating them together as lead salts, directly estimating the one and arriving at the other by difference, then the importance of settling the point becomes apparent.

The method of analysing the lead tungstate may be as well described at the outset. The principle involved will be made—has already been made in fact—the basis of a separation of tungsten and molybdenum.

On boiling ignited lead tungstate with a large excess of concentrated hydrochloric acid it is dissolved to a clear solution. On continued boiling an opalescence forms, deepens, and would become yellow through precipitated tungstic trioxide. Before this point is reached, providing only that the solution be opalescent, dilution with four or five times the acid's volume of water, and subsequent boiling for a few minutes, throws down *all* the tungsten as trioxide. This precipitate is soluble in concentrated hydrochloric acid, it is very easily filtered, and unless the turbidity, previous to the addition of water, has become yellow it does not stick to the sides of the beaker. The addition of nitric acid throws down WO_3 even from the concentrated hydrochloric solution, but generally its presence causes an irremovable deposit on the sides of the beaker. It might also be found that simply boiling with dilute hydrochloric acid would decompose the lead tungstate, and leave only the WO_3 behind.

After washing the WO_3 with very dilute hot hydrochloric acid (pure water causes it to pass through the filter) pulp and precipitate are ignited together; the residue has a beautiful pale yellow colour. In the filtrate the lead may be determined by neutralising with ammonia, making acid with acetic, and precipitating with a perfectly clear solution of sodium or ammonium molybdate in the manner previously described (Chemical News, lxx. x., 14).

The difficulty of working through a series of operations in *perfectly* neutral solutions is well known. The presumed analogy was therefore tested in the first place by observing the precipitation of lead tungstate in a solution acidified with acetic.

Since approximately pure alkaline tungstates are difficult to obtain, and as according to Smith and Oberholtzer (Chemical News, lxviii., 6) and other authorities the purest tungsten compounds obtainable, even the "wolframsaure puriss" contain molybdenum, the standard solution was prepared from a carefully analysed metallic tungsten powder. Previous to fusion with soda carbonate it was ignited for a long time, so as to volatilise any Mo or MoO_3 which it may have contained. I have to thank Mr. R. L. Leffler for repeatedly confirming the strength of my standard solutions by an independent method.

The amount taken for each test should theoretically yield 0·2588 grm. of $PbWO_4$. The ratio $PbWO_4 : WO_3$, by which, after analysis, the nature of the compound is determined, is 1·962 if Pb = 207, W = 184, and O = 16.

The Influence of Acetic Acid.

With an excess of only 1 c.c. of acetic acid in a solution measuring about 300 c.c., the $PbWO_4$(?) after ignition weighed only 0·2384 grm., and yet on analysis yielded an amount of WO_3 (0·1320 grm.), corresponding exactly to the theoretical amount (0·2588 grm.) of lead tungstate. Here the ratio $PbWO_4 : WO_3$ is only 1·806. A like result repeated itself with each successive experiment carried out in a similar way. Finally by precipitating with a known amount of lead and estimating the excess a similar result was arrived at. The excess and that combined with the WO_3 making up the amount added, but both alike pointing to the acid character of the precipitated lead tungstate. Thus test upon test showed that in what might be called a faintly acetic solution of alkaline tungstate, the precipitate formed by lead acetate is never $PbWO_4$, but an acid compound $PbWO_4.xWO_3$.

Experiments carried out in more strongly acidified solutions gave the following results:—

Excess acetic.	Grs. $PbWO_4$ (?).	Grms. error.	WO_3 obtained on analysis.	$\frac{PbWO_4\ (?)}{WO_3}$.
1	0·2384	0·0204	0·1320	1·806
10	0·2190	0·0398	0·1305	1·678
30	0·1900	0·0688	0·1210	1·570

By very long-continued boiling a further precipitate could be formed in the very acid filtrate from the lead tungstate, but it was only small compared with the deficiency, and any hope of completing the precipitation is never likely to be realised in that way.

The acid character of precipitated lead tungstate is not peculiar to acetic solutions. It seems generally to be the case if the precipitation is performed in an acidified medium. Thus if a solution of alkaline tungstate be faintly acidified with nitric acid, as is customary when precipitating tungsten with mercurous salts* (Blair, "Chem. Anal. of Iron," p. 193) and precipitated with a solution of lead nitrate, using mercuric oxide to destroy the last traces of acid, the resulting lead tungstates are decidedly acid. Of the following, Example I. contained a large amount of ammonium nitrate, II. contained none.

	Grs. $PbWO_4$ (?).	Error.	WO_3 on analysis.	$\frac{PbWO_4\ (?)}{WO_3}$.
I.	0·2460	0·0128	0·1310	1·878
II.	0·2270	0·0318	0·1320	1·720

One of the precipitates contains precisely, and the other nearly, the whole of the added tungsten, in spite of the enormous deficiency of the weighing as $PbWO_4$.

Now that the acid character of lead tungstate formed under these circumstances has been established, the fact does not seem so surprising, except in its intensity, nor is an explanation far to seek. The peculiarity would seem to depend entirely on the fact that lead tungstate is easily decomposed by very dilute acids, and that its formation in an acidified solution offers the most suitable occasion for illustrating this. In order to further elucidate the point a series of experiments were performed under the same conditions as those of Table I., except that instead of adding the lead acetate to a hot acid solution of the alkaline tungstate it was added to a slightly alkaline solution, the excess of acetic acid being added later; in this way was formed a true, or probably a somewhat basic lead tungstate. The results tabulated show that, besides decomposing lead tungtate, the larger amounts of acetic acid either dissolve some of the liberated WO_3 or else dissolve some of the lead tungstate undecomposed.

Excess acetic.	Grs. $PbWO_4$ (?).	WO_3 on analysis.	$\frac{PbWO_4}{WO_3}$.
1	0·2430	0·1320	1·841
10	0·2320	0·1314	1·766
30	0·2160	0·1280	1·687

Precipitation of Lead Tungstate from Neutral Solutions.

Neutral alkaline tungstates precipitated with neutral lead acetate invariably gave precipitates which were

* The results being given raise the question as to whether or not the precipitate is accurately described as "mercurous tungstate." The question has no bearing on the results obtained, as all the mercury is volatilised on ignition, and the tungsten calculated from the remaining WO_3.

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somewhat basic. The error was generally about 2 per cent. The ignited precipitates always yielded on analysis as much WO_3 as corresponded to the amount of material taken.

The excess of PbO may be due either to the decomposition of the excess of lead acetate into acetic acid and lead protoxide, a change acetates in hot neutral solutions are very prone to (see Watts's "Dictionary," vol. i., p. 9, and CHEM. NEWS, lxxvi., 223), particularly when a precipitate is being formed in their solution; or, as has been pointed out (Watts's "Dictionary," i., 11), the aqueous solution of lead acetate is partially decomposed by the CO_2 of the air, lead carbonate being precipitated, and a portion of acetic acid set free. Alkaline tungstates, too, are never perfectly free from CO_2, and, further, the neutralisations in presence of large amounts of alkaline salts, using methyl orange as indicator, is, according to Thomson (CHEM. NEWS, xlvii., 126), not quite coincident with actual neutrality; so that absolutely neutral solutions are only obtainable with difficulty, and even then the correct precipitate is not assured.

Working still in neutral, or as near as practicable neutral, solutions, the influence of various alkaline salts, since they always accumulate in an analysis, was observed.

Am. chloride. Grs. added.	$PbWO_4$.	Error.	WO_3 on analysis.	$\frac{PbWO_4}{WO_3}$
2	0·2155	0·0433	0·1120	1·920
5	0·1580	0·1008	0·0805	1·963
Am. nitrate.				
2	0·2580	0·0008	0·1314	1·963
5	0·2540	0·0048	0·1315	1·931

Acetate exerts a decidedly solvent action, but not nearly so marked as the chloride. The results show that ammonium chloride should always be avoided. The results with ammonium nitrate are in general agreement with those of Smith and Bradbury (*Berichte*, xxiv., 2093), who found $PbWO_4$ to be insoluble in solutions of that salt. The acidity of the lead tungstate in the first and last results are certainly not due to any peculiar influence exerted by those particular amounts of salts, but probably to an imperfect neutralisation. It is scarcely credible what small amounts of acid affect the basicity of the precipitates.

As many compounds of tungsten must be attacked by fusion, the influence of salts of the fixed alkalis are appended.

Soda chloride. Grs. added.		$PbWO_4$.	Error.	WO_3 on analysis.	$\frac{PbWO_4}{WO_3}$
2	(*a*)	0·2550	−0·0038	0·1295	1·969
	(*b*)	0·2620	+0·0032	0·1310	2·000
5	(*a*)	0·2020	−0·0568	0·1010	1·974
	(*b*)	0·2110	−0·0478	0·1050	2·009
Soda nitrate.					
2		0·2570	−0·0018	0·1310	1·962
5		0·2540	−0·0048	0·1310	1·939
Potass. nitrate.					
5		0·2594	0·0006	0·1312	1·979

Soda chloride exerts a remarkable influence. Up to about 2 grs. (vol. of solution 300 c.c.) the error introduced is not very great, and under some circumstances would be allowable. In the sample containing 5 grms., however, the filtrate on re-boiling becomes cloudy with a further precipitate, and successive precipitates may be formed and filtered off time after time, but never when aggregated do they approximate theoretical demands so nearly as would make the presence of soda chloride with long boiling tolerable. In the table samples (*a*) were just raised to boiling, (*b*) were boiled several minutes. The precipitates of the latter are decidedly basic.

How shall the precipitation of tungsten as a lead salt be made available for accurate analytical purposes? It is of little moment whether the precipitate have an acid or a basic character so long as it contains the whole of the tungsten, if one cares to go a step further and separate the WO_3 by treatment with hydrochloric acid, &c. To this end the precipitation may be made from a solution acidified slightly with acetic acid, or with nitric acid using mercuric oxide to take up the excess, or even from a solution made faintly alkaline with or without the further addition of acetic. In any case the tungstic acid will be an accurate measure of the tungsten originally present.

To throw down the tungsten under such conditions as would assuredly lead to an ignited precipitate which was really $PbWO_4$ was the object in view when the influence of ammonium chloride was observed. As that salt is not available, ammonium nitrate must be made to serve the same purpose. On adding lead acetate to an ammoniacal solution of dilute ammonium chloride or nitrate, the basic precipitate which forms in the cold is completely dissolved as the excess of ammonia is driven off by boiling. If, then, to the alkaline tungstate there be added 2 or 3 grms. of ammonium nitrate, a faint excess of nitric acid (boil a few minutes), a small excess of ammonia, and an excess of lead acetate, we shall have formed $PbWO_4$ mixed with a little basic lead compound. This latter body is redissolved by a few minutes' brisk boiling, and the true $PbWO_4$, which becomes denser by the boiling, may be filtered off, ignited, and its weight used for the calculation of the tungsten.

The following are a few such tests calculated, I. from the weight of $PbWO_4$, and II. from the WO_3 obtained after decomposing that precipitate with hydrochloric acid.

Tungsten added. Grs.	Tungsten found. I.	II.
0·2093	0·2081	0·2086
0·1046	0·1043	0·1044
0·0523	0·0526	0·0522
0·0209	0·0212	—

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PREPARATION OF ARSENIC HYDRIDE.

By A. P. SAUNDERS.

HAVING occasion some time ago to prepare considerable quantities of the hydride AsH_3, the writer devised a method based on that of Janowsky (*Ber.*, vi., 219), but differing from this in certain particulars, which make it perhaps worth noting.

The method of Janowsky consists in first preparing arsenide of sodium by passing the impure hydride obtained from zinc arsenide and sulphuric acid over heated sodium, and then decomposing this compound by means of water or dilute acid. This method of preparing the arsenide of sodium is, however, difficult and tedious. A much simpler way is by heating together the two elements in question. This is effected in the following manner:—A porcelain boat is filled with arsenic in powder or very small fragments, and upon it are placed a few small pieces of freshly-cut sodium; the boat is then immediately placed in a piece of wide combustion-tubing, protected inside by a strip of asbestos upon which the boat is placed. The ends are loosely plugged, and the tube then slowly heated with a burner. When the heating has been carried up to such a point that the glass just begins to redden, the reaction takes place suddenly and with great violence, so that the glass tube is not unfrequently cracked; for such emergencies it is well to have a large vessel of copper sulphate solution at hand in the hood, since arsenide of sodium is at once decomposed by moisture forming the hydride. If the operation is successful, the tube may be closed and laid aside to cool. The reaction is somewhat cleaner if carried on in a stream of hydrogen, but, as a little sodium oxide or hydroxide does not finally affect the result, this precaution is unnecessary.

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A convenient form of apparatus for generating the gas may be made by sealing on to a wide tube, ending above in a stopcock, a side tube set on at an angle, and sufficiently large to allow the porcelain boat with its contents to fall freely through it into the bottom of the main tube. Such an apparatus is first filled with dilute hydrochloric or sulphuric acid, and the boat is then allowed to drop in by the side tube: the gas generated collects in the top of the main tube, and may thence be transferred to other vessels.

In filling the boat care must of course be taken that arsenic shall be present in considerable excess, so that no free sodium may remain.

In using this method no effort was made to get the gas quite free from hydrogen; nevertheless it appeared, by absorption with copper-sulphate solution, to be over 90 per cent pure; hence the method could probably be modified to produce the hydride in almost or quite pure condition.

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GÜNZBURG'S REAGENT APPLIED TO THE DETECTION OF HALOGENS IN ORGANIC COMPOUNDS.

By P. N. RAIKOW.

About ten years ago Günsburg proposed the use of an alcoholic solution of phloroglucine and vanilline for the detection of free hydrochloric acid in the gastric juices.

This reagent remains unchanged by heat, under the influence of the organic acids, while even a trace of free hydrochloric acid is sufficient to cause an intense red colouration.

The mixture of phloroglucine and vanilline can also be used for the purpose of detecting the presence of halogen bodies in organic substances; but it must be mentioned that these combinations, heated directly with the reagent, rarely give the characteristic red colouration. But in submitting the products of the combustion of the organic halogen compound to careful examination, we can detect with certainty the least trace of the haloid acids formed.

When the organic matter is liquid and inflammable, a small quanitity is placed at the bottom of a flat porcelain dish, a few drops of the reagent are added, and the alcohol set alight. In the case where the substance is a halogen compound the contents of the crucible take an intense red colour, but when halogens are absent no colouration is noticeable.

Thus, for example, we can recognise with certainty the presence of halogens in the following substances:—$CHCl_3$, CCl_4, C_2Cl_4, C_6H_5Cl, and $C_6H_4Br.CH_3$; but in some compounds, such as C_6Cl_6 and $3C_6Cl_4O_2$, we cannot detect chlorine by this method.

We can, however, detect the presence of haloid bodies in all halogen compounds by proceeding in the following manner:—Rinse a small porcelain crucible with the reagent, throw away the excess, and set light to the small quantity of alcohol remaining in the crucible, or it can be left to spontaneous evaporation.

The phloroglucine and the vanilline which were in solution remain in the crucible in the form of a thin colourless layer. Turn the crucible upside down over a spirit lamp, so that the flame licks, so to speak, the layer of phloroglucine-vanilline, and, by the aid of a copper or platinum wire, hold a small quantity of the substance under examination in the flame. If a haloid body is present, the characteristic colouration will be produced in the crucible.

When the subject of examination is a gaseous body, two cases may occur. Either the gas is inflammable, when it can be lighted at once; or it is not inflammable, and it must be brought into the flame of the spirit lamp over which the crucible containing the layer of phloroglucine-vanilline is held.—*Chemiker Zeitung*, 1898, No. 4, p. 20.

DETERMINATION OF THE SOLIDIFICATION-POINT OF PARAFFINS.

By R. KISLING.

In commercial transactions it is the solidification-point that is chiefly considered in estimating the value of paraffins; the other factors—such as colour, odour, transparency, &c.—play only a secondary part.

Numerous methods have been proposed for determining the point of solidification of paraffins, but such care must be taken, and so many precautions are necessary, that they lose much of their value and simplicity.

For this reason I have devised a new method, at once simple and exact, and which does not take longer than ten minutes to perform. The only fault that can be found with my process is that it requires at least 50 grms. of paraffin to carry it out.

The apparatus I employ consists of a glass cylinder we will call A, 12 c.m. high and 8 c.m. in diameter; a flat piece of wood or cardboard is placed on this cylinder, and has a central hole, destined to hold a precipitation glass, which we will call B; its height is about 8 c.m. and its diameter about 5 c.m.

In B we place 50 grms. of clear paraffin, filtered if necessary; heat on the water-bath to a temperature of about 10° higher than the solidification-point of the paraffin, and place it in the larger cylinder in such a manner that it is suspended by its rim in the hole through the cardboard. The melted mass is stirred by means of a thermometer until a small pellet of solid paraffin is formed in the centre of the bottom of the glass. We may be sure that the solidification-point has now been reached, because immediately afterwards the whole of the bottom of the glass becomes covered with a thin layer of solid paraffin in such a manner that streaks may be made with the thermometer. At the same time flakes of paraffin appear throughout the mass. The test may be repeated several times with the same sample.

To catch the critical point exactly, it is better to look through the side of the glass rather than down from the top.

The results obtained are perfectly concordant, and do not vary by one-tenth.

I may point out that the method is equally applicable to the determination of the point of solidification of ceresine, stearine, and solid fats, &c.—*Chemiker Zeitung*, 1898, p. 209.

THE COLORIMETRIC ESTIMATION OF COPPER.

By M. LUCAS.

A solution of a copper salt gives a reddish-brown colouration with ferrocyanide of potassium. If the solution is weak the precipitate will only collect very slowly, and leaves the solution clear, but of a red colour. It is this colouration, ten times more sensitive than that given by ammonia, that can be utilised for the estimation of small quantities of copper.

M. Jagnaux has shown (*Anal. Chim.*, p. 451) that it is necessary to treat acid solutions of copper with ammonia, and to boil them until they have a neutral reaction. Then place a few drops of ferrocyanide of potassium in two test-tubes, pour into one a known volume of the solution to be examined, and bring the liquid in both test-tubes to the same level by adding distilled water; add 0·5 grm. of nitrate of ammonium, then, to the tube containing distilled water, add a titrated solution of copper until the

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tints in the two test-tubes are identical. The tests are made under the following conditions:—

1. The solution under examination contains more nitrate of ammonium than the tube for comparison.
2. The ferrocyanide of copper is in one case formed in a small volume of liquid; the solution, then diluted, gives a different colouration to that which is obtained in the definite volume.
3. Nitrate of ammonium added after the reaction does not change the colour, though if added beforehand it gives a milky rose-coloured appearance, a more intense colouration, and a precipitate which collects very rapidly.
4. If the solution to be examined contains hydrochlorate of ammonium, boiling causes a loss of copper; if it contains nitrate of ammonium, the copper may be precipitated in the state of basic nitrate, and will no longer give a uniform colouration.

Sufficiently accurate results can be obtained by always working under the same conditions; a scale of comparative colours can be made by adding the same volume of nitrate of ammonium as there is in the solution being tested, and diluting to the same volume; the ferrocyanide of potassium is added to all the tubes simultaneously, and the colourations are compared immediately. It is, however, better to prevent the presence of other salts by evaporating the hydrochloric solutions to dryness, taking up with water, and titrating from a burette filled with the typical solution containing 1/10,000th of bichloride of copper. In this manner I obtained the following results:—

	1.	2.	3.	4.	5.	6.	7.	8.	9.	10.
Amount taken	5·0	7·0	5·0	4·0	3·5	9·0	5·0	3·5	8·5	8·3
Amount found	4·8	6·5	5·0	4·0	3·8	8·5	5·0	3·0	8·0	8·0

I have applied this method to the estimation of oxygen in commercial copper.

a. Estimation of Oxygen in Copper.—The metal is treated with nitrate of silver, and the precipitate, separated from the filter in the way I have described in a previous communication, is treated with a boiling solution of hydrochloric acid at 5 per cent.; this dissolves the basic nitrate of copper: filter, evaporate to dryness with a few drops of sulphuric acid, take up with nitric acid, separate the copper by electrolysis, dissolve it in nitric acid, evaporate to dryness with hydrochloric acid, take up with 100 c.c. of water, and add 5 drops of a 5 per cent solution of ferrocyanide of potassium.

To 100 c.c. of water and 5 drops of ferrocyanide of potassium add, with a graduated burette, a solution of bichloride of copper (Cu = 0·1 grm. per litre) until the colour in each tube is identical, taking care to keep the two liquids at the same volume.

The number of c.c. of bichloride of copper run in represents the number of tenths of a m.grm. of copper.

Electrolysis seemed to me to be necessary for separating the copper from the iron; it is the only possible method when using sulphydric acid at 70°. Separation by ammonia, even when repeated several times, is incomplete, but this inconvenience would be negligible. It, however, introduces salts of ammonia, which, it is true, can be reproduced in the comparative tubes, but this is nevertheless very unfavourable to the reaction; they cannot be driven off by volatilisation without causing a loss of copper.

b. Estimation of Copper in Wrought Iron, Steel, and Iron Castings.—The copper, electrolysed directly in nitric solution, is re-dissolved, and electrolysed a second time to separate all traces of ferric oxide.

This deposit is estimated colorimetrically by the same method as in *a*; the electrolysis of 1 grm. of metal may give a deposit of less than 1 m.grm. of copper.—*Bull. Soc. Chim.*, Series 3, vol. xix.-xx., No. 18-19.

ON THE CAUSE OF THE RETENTION AND RELEASE OF GASES OCCLUDED BY THE OXIDES OF METALS.*

By THEODORE WILLIAM RICHARDS.

(Concluded from p. 53).

It is obvious that, if the oxide is really dissociated, it should be capable of conducting electricity, because of the presence of traces of metal. In order to test this point, small platinum electrodes of 0·25 square c.m. in area and separated from one another by about 0·5 c.m., were packed in pure specimens of the several oxides. Each porcelain crucible containing an oxide was gradually heated, after having placed the two electrodes in a circuit with a delicate amperemeter and four accumulators. When cold, the resistance of each of the oxides was at least 200,000 ohms. Upon heating, the cupric oxide began sensibly to conduct below a red heat, and at about 650° offered only about as much hindrance to the current as was afforded by 550 ohms, remaining constant at that point. On the other hand, zincic oxide fell in resistance only to about 15,000 ohms at 650°, and required fully 900° to bring it as low as 1000 ohms; while the highest heat of the blast-lamp could not cause the magnesic oxide to transmit as much as the twentieth of a milliampere, the least current capable of being observed upon the amperemeter. It is needless to say that any possibility of the presence of a reducing atmosphere was excluded, and the fact that each oxide returned almost if not quite to its non-conducting state after cooling is sufficient proof that the heat alone was the cause of the phenomena observed. These interesting results are fully in accord with the hypothesis that cupric oxide is slightly dissociated at a red heat, that zincic oxide is less dissociated, and that magnesic oxide, retaining its occluded oxygen with great obstinacy, is scarcely dissociated at all. Magnesic oxide, being one of the stablest of all compounds at high temperatures, could not be expected to show any appreciable dissociation or conductivity; and the wonder is, that the occluded gas is able to escape even as fast as it does.

This assumed partial thermal dissociation of solids must not be confounded with electrolytic dissociation (ionisation); for the energy which determines the separation of the components in the present case is heat, and not electricity. The conductivity is not electrolytic conductivity, but only the metallic conductivity of the metal set free by a purely thermal dissociation. In order to prove this, a current of 20 milliamperes was transmitted through cupric oxide for three hours. This quantity of electricity would have carried nearly 70 m.grms. of copper from a cupric solution, and since neither copper nor an oxide appeared adhering to the platinum negative electrode, it is safe to infer that the conductivity is not electrolytic. While these oxides thus conduct electricity without transference of material, it is undoubtedly true that many substances—even glass for example—which are non-conductive when cold, become capable of carrying a current *electrolytically* when heated. Melted salts are well known to be good electrolytic conductors, and Graetz (*Wied. Ann.*, 1890, vol. xl., 18), has found that this conductivity begins before the salts have melted. Our knowledge of the *rationale* of these facts is altogether too incomplete to afford satisfactory explanation of all the phenomena attending the passage of electricity through solids, liquids, or gases at high temperatures; and it is perhaps unsafe to record the conductivity of cupric oxide as a definite indication of the temporary presence of metallic copper in the case under discussion.

Following is a more certain proof that this dissociation is to be considered as analogous to the decomposition of

* Contributions from the Chemical Laboratory of Harvard College. From the *Proceedings of the American Academy of Arts and Sciences*, xxxiii., No. 22; also *American Chemical Journal*, November, 1898.

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limestone by heat. Here, as there, the gas, in the present case oxygen, must have a definite pressure of dissociation; but no appreciable amount of metal or lower oxide can form when the tension of the oxygen in the surrounding atmosphere is greater than this definite pressure. On the other hand, cupric oxide should lose not only its occluded oxygen, but all the oxygen that normally belongs to it, leaving metallic copper (or at least cuprous oxide), when heated in a perfect vacuum or in an inert atmosphere, if the hypothesis under consideration is tenable. This begins even in the air at about 1000°. The search in chemical literature revealed a statement by Hilditch that cupric oxide ignited at lower temperatures in a vacuum weighs less than it did before, as well as one by Morley that the same substance slowly evolves a gas when heated in a vacuum (Hilditch, Chem. News, 1884, vol. xlix., 37; Morley, *Am. Journ. Sci.*, 1891, xli., 231). Since it is hard to tell whether this evolution might not be merely that of the occluded gases, it was thought worth while to repeat the experiment.

Two grms. of cupric oxide, which had been ignited for a long time in pure air until constant in weight, were found to evolve a gas steadily when heated in a vacuum to about the melting-point of common salt (790°), provided that the gas was removed by a Sprengel pump as fast as it was formed. When allowed to attain equilibrium, this gas (which repeated analysis showed to be almost pure oxygen, containing only traces of nitrogen and carbon dioxide) was found to possess a tension of two- or three-tenths of a m.m. of mercury. A portion of the same material was heated for many hours more in a crucible to a full red heat; but upon subsequently heating it in a vacuum the evolution of gas proceeded just as before. Since all the occluded oxygen except 2 or 3 per cent had been expelled by the preliminary heating, this must have been structural oxygen. The conclusion was confirmed by the discovery of red cuprous oxide in the residue. Repetitions of the experiment showed that the tension of the gas increased enormously with the temperature, exceeding a m.m. before the glass became so soft as to collapse. In some of the experiments the best Bohemian glass was used, in others the hardest made in Jena, The nature of the glass seemed to be without influence on the result. The amount of gas evolved in a given time naturally depends upon the efficiency of the pump, as well as upon the temperature; in one of the experiments 2 c.c. of oxygen were obtained in eight hours.

Ignition of the substance in an inert atmosphere should produce the same effect. Since cupric oxide is slightly dissociated by heat, perceptible amounts of oxygen should be removed by heating it in nitrogen, just as carbonic acid is removed from limestone by heating it in a current of air. This dissociation of cupric oxide must have its effect on any process involving the ignition of cupric oxide in a vacuum or in an inert gas. The determination of organic nitrogen by means of the Sprengel pump, for example, must be affected by it. The use of carbon dioxide as a displacing medium in the Dumas method probably disposes of the error, however; for carbon dioxide is itself dissociated by heat, and it undoubtedly furnishes enough oxygen to diminish greatly the decomposition of the cupric oxide.

In the light of these results it is obviously advisable, when one desires to remove oxygen from a mixture of gases by means of hot copper, to maintain the last portion of the tube at a comparatively low temperature. Even then the issuing gas may not be absolutely free from oxygen.

Everyone knows that auric oxide is excessively unstable, and that argentic oxide is completely decomposed even in an atmosphere of pure oxygen at comparatively low temperatures. The present results merely extend this behaviour, in a much smaller degree, to cupric oxide, and the hypothesis carries the idea still further. The dissociation of zincic oxide must of course be yet less, while the tension of oxygen above magnesic oxide even at high temperatures must be an infinitesimal far less in value than the tension of the gas in the vacuum needed for the production of X-rays.

According to the phase rule and the law of mass action these reactions must take place in the gaseous phase,—the only one present of variable composition. As an example, the case of copper is given below:—

$$\underset{\text{Vapour.}}{4CuO} \rightleftharpoons \underset{\text{Vapour.}}{2Cu_2O} + \underset{\text{Gas.}}{O_2}$$

$$\uparrow\downarrow \qquad\qquad \uparrow\downarrow$$

$$\underset{\text{Solid.}}{4CuO} \qquad\qquad \underset{\text{Solid.}}{2Cu_2O}$$

The occluded oxygen is supposed to escape by the oscillation, backward and forward, of this heterogeneous reaction. The ability of the system to be first dissociated and then associated in another place where more oxygen is present presupposes, however, great internal activity in the substance of the hot solids; and this internal activity is the most interesting conclusion to be drawn from the phenomena under discussion.

In short, no matter what point of view one adopts, or what mechanical picture one forms of the reaction, the necessity of ascribing the rapid escape of the oxygen to internal re-arrangement seems to be inevitable.

Professor Morse, in another letter received since the foregoing was written, kindly tells me that, in the course of some admirable work upon the atomic weight of cadmium which he has just completed, he has had occasion to measure the gases occluded by cadmic oxide made from the nitrate. As one would expect, this oxide holds its occluded oxygen more firmly than copper, but less firmly than zinc. In fact, the behaviour of the substance, according to Professor Morse's description, probably accords well with the hypothesis under consideration. His interesting results will soon be in print, and will speak for themselves. The fact that Rogers and I found no gas in our cadmic oxide in 1892 is easily accounted for by the circumstance that we used a bright red heat in the ignition the oxide parting with both gases by the disintegration of its original structure, as the oxide of copper did with Scott. Since cadmium is volatile at high temperatures, however, it was natural that its dissociated oxide should have a wider opportunity of re-arrangement than in the case of copper; and hence the crystalline structure of the ignited oxide observed in 1892. Nickel, another metal whose oxide was investigated by Rogers, probably occupies its expected place near cadmium, as far as its oxide's capacity to retain oxygen is concerned. In some recent experiments in this laboratory, Cushman succeeded in partially decomposing nickelous oxide in a stream of nitrogen below 1200°. All these considerations are concordant with the hypothesis devised to explain the escape of occluded oxygen for metallic oxides.

The only point regarding this occlusion of gases left unexplained is the fact that in the experiments of Morse and Arbuckle the total amount of gas was in every case nearly the same, although the proportion of oxygen and nitrogen varied. This is a very interesting circumstance. The experimenters ignited their oxide to constant weight,—in other words, until two successive ignitions caused no appreciable change; but it does not follow from this that the evolution of gas had ceased,—one can only maintain that it had become so slow as to be inappreciable. Evidently, then, the question to be answered is, Why has the oxygen more difficulty in escaping when a small amount of nitrogen is present than when a large amount is present? The reason of this eccentricity may be because those specimens which contain the most gas are naturally the most porous and loosely held together, although usually formed in larger individual aggregations; and the freer atomic and molecular motion allowed by the looser structure permits the oxygen to leave more rapidly. Hence in each case the sum of the oxygen and nitrogen amounted

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to about the same volume. This hypothesis within an hypothesis is rather too uncertain to deserve much emphasis, however.*

In the course of some of my old experiments on the impurities in cupric oxide, it became necessary to reduce the substance in a current of carbon monoxide. Referring to this work Dr. A. Scott, in the paper already cited (*Proc. Amer. Acad.*, xxvi., 563), expresses surprise at the existence of an admixture of hydrogen in this gas. His experience agrees with that of Stas in finding only a small amount of such gaseous impurity in carbonic oxide obtained from oxalic acid, while my results indicated a large amount. Lord Rayleigh, in the course of his recent work on the density of gases (*Proc. Roy. Soc.*, 1898, lxii., 204), concludes that his carbonic oxide also was free from hydrogen or hydrocarbons; and indeed there is no reason why this result should not be easily attained if one uses pure materials. Lord Rayleigh explains the existence of hydrogen in my carbonic oxide by drawing attention to the fact that in my case the gas, dried only by calcic chloride, was passed over red-hot platinum sponge.

This explanation is undoubtedly correct. Many experimenters have shown that the reaction—

$$CO + H_2O = H_2 + CO_2$$

is an easily reversible one at high temperatures (Bunsen, *Liebig's Annalen*, 1853, lxxxv., 137; Horstmann, *Ibid.*, 1878, cxc., 228; Bötsch, *Ibid.*, ccx., 207; and especially Hoitsema, *Zeitschr. Phys. Chem.*, xxv,, 688, as well as others), and in the presence of a large excess of carbon monoxide, it is obvious that nearly all of the trace of aqueous vapour would be reduced. For my purpose at the time, the source of the hydrogen was of no importance; it was only necessary to know the exact amount of the impurity, and this was suitably determined. It is satisfactory to know the cause of the discrepancy, however, as well as to know that it is easier to prepare carbon monoxide almost free from hydrogen than seriously contaminated with it. More often than we suspect, perhaps, are our carelessly planned efforts at purification apt thus to introduce more impurity than they eliminate.

In a recent number of the *Journal of the American Chemical Society* (March, 1898) F. R. M. Hitchcock has published a preliminary paper upon the occlusion of various gases by the oxides of metals, having apparently overlooked the Harvard investigations. It is satisfactory to see the phenomenon widely recognised; for an appreciation of this serious cause of possible constant error will result in the publication of fewer erroneous determinations of atomic weights than have appeared in the past. One should also bear in mind the fact that nitric acid is not by any means the only substance which is liable to leave appreciable contamination in material from which it has been expelled by heat. The number of such occlusions is far greater than most analysts imagine; this fact is not realised because the minute residues are often so hard to detect.

The evidence of this paper proves that in reality no discrepancy exists between the results of Scott, and Morse and Arbuckle, and those obtained at Harvard. The apparent disagreements were caused by the fact that the later experimenters investigated parts only of the wide field outlined in 1892, the relation of the parts to the whole being partially unperceived. The paper also shows that the unequal escape of oxygen and nitrogen imprisoned in the oxides of metals is a phenomenon of great interest, capable of shedding light on the internal kinetics of solids.

* In this connection it is a matter of interest to note that Ramsay (*Phil. Mag.*, 1894 [5], xxxviii., 206) has found that the presence of nitrogen in a palladium bulb seems to prevent to some extent the diffusion of hydrogen into it. This observation is not unlike Morse and Arbuckle's; but if, as a matter of fact, an indifferent gas can produce such an effect, our present notions concerning semi-permeable septa demand some revision.

NOTICES OF BOOKS.

Text-book of Zoology. By H. G. Wells, B.Sc. Lond., F.Z.S., F.C.P., and A. M. Davies, B.Sc. Lond. The University Tutorial Series. London: W. B. Clive, University Correspondence College Press. Pp. 366.

This book, though in one way a second edition of Wells's "Text-book of Biology" under another title, has, as a matter of fact, been almost entirely re-written; only one chapter (Chap. XIV.) remains practically the same as in the first edition.

The first twelve chapters are on the rabbit, its digestion, circulation, respiration, tissues, nervous system, reproduction, &c., being in turn all fully described and illustrated.

In Part II. the lower Vertebrata are similarly dealt with; among these we find the frog, the dog-fish, the lancelet, &c.: this part comprises four chapters.

In Part III., in six chapters, we have the development of the Vertebrata, such as the chicken and the rabbit; while in Part IV., consisting of five chapters, the Invertebrata are discussed: these include the slipper-animalcule, the fresh-water polype, the earthworm and crayfish.

At the end of each Part are a number of questions on the particular subjects just gone through. The whole book is arranged with regard to the preliminary and intermediate Science Examinations of the London University.

Photographic Formulæ. ("Ricettario Fotographico"). By Dr. Luigi Sassi. Second Edition, Revised and Enlarged, with New Formulæ and Processes. Milan: Ulrico Hoepli. 1899. Pp. 167.

The first part of this handy little volume describes the obtaining of negatives, their development, toning, fixing, &c., with 112 formulæ. Part II. deals with positive processes, and gives over 95 formulæ; while Part III., and last, consists of miscellaneous methods and items, all of considerable interest to photographers.

The book is primarily intended for the use of amateurs rather than professionals.

Aluminium. ("L'Alluminio"). By Dr. C. Formenti. With 67 Figures and 21 Tables. Milan: Ulrico Hoepli 1899. Pp. 323.

The principal scope of this manual is to fully describe, in a practical and complete manner, the history, minerals, methods of production, properties, uses, commercial value, &c., of this comparatively new metal, aluminium. This is the first work on this subject published in Italy, and the author hopes, as he has good reason to, that it will compare favourably with those published in other countries. The printing, paper, and diagrams leave nothing to be desired.

The Galvanic Deposition of Nickel, Silver, Gold, Copper, &c. ("Galvanostegia, Nickelatura, Argentatura, Daratura, Ramatura"). By I. Ghersi. With Four Illustrations. Milan: Ulrico Hoepli. 1899. Pp. 323.

As its title shows, this book deals solely with the electrodeposition of metals, and includes not only the more well-known ones, but also those which—like palladium, iridium, chromium, molybdenum, aluminium, cadmium, &c.—are less frequently met with. In the Appendix a number of special and experimental baths are described.

Colouring and Decoration by means of Metals, both by Chemical and Electrical Methods. ("Colorazione e Decorazione dei Metalli, per via Chimica ed Elettrica"). By I. Ghersi. Milan: Ulrico Hoepli. 1899. Pp. 190.

The methods of obtaining decorative and coloured effects herein described cover a large field, and have abundant

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applications in modern decorative art. Such processes as are described cannot be adequately illustrated in a book of this size, but the descriptions are full, and should be of great service to those interested in this branch of art.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

NOTE.—All degrees of temperature are Centigrade unless otherwise expressed.

Comptes Rendus Hebdomadaires des Séances, de l'Académie des Sciences. Vol. cxxvii., No. 26, December 26, 1898.

Separation and Estimation of the Halogen Elements in their Silver Compounds.—H. Baubigny.—The author has devised a convenient method of analysing accurately a mixture of silver chloride, bromide, and iodide. He employs an oxidising agent in the presence of an acid, and finds the best results are obtained by using sulphuric acid and potassium bichromate, giving free chromic acid. At ordinary temperatures, the iodide and bromide are transformed into iodate and bromate. The solution of iodate can be filtered off and the iodine and bromine together estimated by the ordinary methods. If the original mixture is heated over a water-bath to 90° or 95°, bromine and chlorine are liberated, the iodate alone remaining unaltered. This can be filtered off and the iodine estimated.

Action of Oxidising Agents on certain Fatty and Aromatic Amines.—Œschner de Coninck and A. Combe.—The action of chromic acid and potassium bichromate in concentrated aqueous solution on the chlorhydrates of methylamine and ethylamine was investigated. Decomposition slowly took place under certain conditions with evolution of CO_2, Cl, and N. Analysis of the gases by the usual methods points to the following equations for the two cases:—1. $CH_3NH_2.HCl+5O = N+3H_2O+CO_2+Cl$; 2. $C_2H_5NH_2.HCl+8O = N+2CO_2+4H_2O+Cl$. The oxidation of several aromatic amines was also effected, with the result that pure CO_2 was evolved. The conclusions drawn are that, in the presence of energetic oxidising agents fatty amines decompose gradually, whilst aromatic amines are decomposed rapidly, with production of CO_2, their nitrogen remaining in combination in the molecule of coloured derivatives which arise.

Thermal Investigation of Normal Propylmalonic Acid. Heat of Formation of the Potassium Salt in the Solid State.—G. Massol.—The acid was prepared synthetically by the action of normal propyl iodide on the sodio-malonic ester, and purified by crystallisation from ether. Melting-point, 93·5°. The following points are enumerated:—I. heat of solution in water. II. Heat of neutralisation by potash in aqueous solution. III. Heat of formation of the solid neutral potassium salt. $C_6H_{10}O_4+2KOH = C_6H_8O_4K_2+2H_2O+46{\cdot}34$ calories.
Solid. Solid. Solid.

Oxidation Products of Oxygluconic Acid.—Léon Boutroux.—The acid was oxidised by nitric acid under conditions favourable to the production of saccharic acid. The result was the production of four acids, viz.:—

COOH	COOH	CH_3	CH_2OH
HO.Ċ.H	H.Ċ.OH	H.Ċ.OH	ĊOOH
H.C.OH	HO.C.H	OH.Ċ.H	
HO.C.H	ĊOOH	ĊOOH	
ĊOOH			
Trioxyglutaric acid.	Racemic acid.	Dioxybutyric acid.	Oxyacetic acid.

which establishes the formula of oxygluconic acid as—

$$CH_2.OH.CO.\overset{OH}{C}-\overset{H}{C}-\overset{OH}{C}.COOH.$$

Journal de Pharmacie et de Chimie, Series 6, Vol. viii., No. 5.

Modification of Mörner and Sjoqwist's Method for the Estimation of the Nitrogen in Urea, or of Urea itself.—H. Moreigne.—The Mörner-Sjoqwist method, which consists in precipitating the nitrogenous principles of urine, other than urea, by adding chloride of barium, baryta, and a mixture of alcohol and ether, is one of the best we possess; but, as described, it can only be employed for certain scientific researches. The author has modified this method, making it more simple and more practical, by suppressing Kjeldahl's operation and estimating the nitrogen of the urea (which is in the residue after evaporation) in the ureometer by means of an alkaline solution of hypobromite of soda.

Volumetric Estimation of the Nitrogen in Urea, or of Urea, by means of an Alkaline Solution of Hypobromite of Soda after Treating the Urine—1st with Phosphotungstic Acid, 2nd with Basic Acetate of Lead and Phosphotungstic Acid.—H. Moreigne.—Normal urine treated with sub-acetate of lead, as is generally done by ureologists, still contains ammoniacal salts, creatinine, and guanine. The latter may be neglected, but it is different with the salts which give up all their nitrogen, and with creatinine which gives up half; thus the nitrogen is considerably augmented, the ammoniacal salts supplying one-eighth or one-tenth of the total. The author has for some years advocated the use of phosphotungstic acid instead of sub-acetate of lead, but now, after having had more experience, he recommends a process in which the basic acetate of lead and phosphotungstic acid are used successively. This method will be fully described in the continuation of the paper.

Microscopic Examination of Wheaten Flours.—E. Colin.—Not suitable for abstraction.

The Direct Synthesis of Anisol and Phenethol.—Ch. Moureau.—A classic method for the preparation of phenols consists in melting the sodium or potassium salts of the sulpho-derivatives of the benzenic hydrocarbides with potash or soda,—

$$C_6H_5.SO_3Na+NaHO = SO_3NaO_2+C_6H_5OH.$$
Benzino-sulphonate of sodium. Phenol.

If, in the above equation, the soda is replaced by methylate of sodium, $NaOCH_3$, we have a new equation, a methyl grouping replacing the hydrogen of the soda—

$$C_6H_5.SO_3Na+NaOCH_3 = SO_3Na_2+C_6H_5.OCH_3.$$

The author thought this reaction might take place in such a way as to furnish anisol by direct synthesis, and experiment has confirmed his expectations. The materials used must be perfectly dry. The mixture of phenylsulphonate of sodium and methylate of sodium in equal molecules is distilled on an oil-bath up to a temperature of 350°, when an oily liquid comes over; this is washed with dilute soda and dried over chloride of calcium. It boils at 152—154°. Analysis shows it to have the composition of anisol. If the methylate of sodium is replaced by ethylate of sodium, phenethol ($C_6H_5.OC_2H_5$) is formed; it is an oily colourless liquid boiling at 168—171°.

The Decomposition of Iodoform in Solution.—J. Bougault.—Two grms. of iodoform, 30 c.c. of ether, and 30 c.c. of a 1 per cent solution of hyposulphite of soda are placed in a flask of about 90 c.c. capacity, the flask is sealed hermetically and exposed to direct sunlight. The solution of iodoform undergoes a rapid partial decomposition; agitate to absorb the iodine, and a further decomposition takes place after a certain time, depending on how often the flask has been shaken. We notice that the ethereal solution of iodoform no longer takes a brown colour, and is no longer decomposed by light; it can now be kept for months without further appreciable decomposition; but if the flask be opened, and a fresh supply of oxygen (air) be allowed to enter, the decomposition recommences at once. The experiment, says the author,

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proves that oxygen intervenes in the decomposition of solutions of iodoform exposed to light. The solution of hyposulphite of soda can be replaced by any other substance which absorbs iodine and which has no action on iodoform, such as mercury or finely-divided silver.

The Reagents for Cotton Seed Oil.—Kiamil Mazar.—Comparative experiments on over 300 samples of oils lead the author to the conclusion that nitric acid (5 c.c. of oil and 10 c.c. of acid at 1·40 free from nitrogen) gives uncertain results. Hirschsohn's reagent (5 c.c. of oil and 10 drops of a chloroformic solution of chloride of gold at 0·5 per cent) is not sensitive. Becchi's reagent (5 c.c. of oil and 25 c.c. of absolute alcohol, and 5 c.c. of a 1 per cent solution of nitrate of silver in absolute alcohol) gives doubtful results. He only finds Halphen's reagent satisfactory, which consists in using equal parts of oil, amylic alcohol, and sulphide of carbon saturated with sulphur.

MISCELLANEOUS.

Royal Institution.—A General Monthly Meeting of the Members of the Royal Institution was held on the 6th inst., Sir James Crichton-Browne, M.D., F.R.S., Treasurer and Vice-President, presiding. The following were elected Members:—G. C. Cathcart, Hon. Alan de Tatton Egerton, M.P., Sir Francis Henry Evans, K.C.M.G., M.P., J. G. Glover, J. W. Gordon, J. Gretton, J. Gretton, jun., M.P., C. E. Groves, F.R.S., and A. Ritchie, J.P. The special thanks of the Members were returned to Professor Dewar for his donation of £100, and to Mr. Frank Clowes for his donation of £10 10s. to the fund for the promotion of Experimental Research at Low Temperatures. The special thanks of the Members were returned to Mr. C. E. Melchers for his donation of £50 for alterations in the Lecture Theatre.

The Late Duke of Northumberland and the Royal Institution—At the General Monthly Meeting of the Members of the Royal Institution, held on February 6th, the following resolution was proposed from the chair by Sir James Crichton-Browne, M.D., F.R.S., the Treasurer, seconded by Sir Frederick Bramwell, F.R.S., the Honorary Secretary, and unanimously adopted:—"The Members of the Royal Institution of Great Britain in General Meeting assembled desire to express to his Grace the Duke of Northumberland their sympathy with him and his family in the loss which they, as well as the Royal Institution and the country at large, have sustained by the death of his father, the late Duke. They desire also to record their grateful sense of the invaluable services rendered to the Royal Institution by the late Duke during his membership of 48 years' duration, during seven terms of office as Visitor and Manager, and as President for 26 years, by his active and unfailing interest in its affairs, and in the progress of science, which it is its object to promote; by his generous benefactions to its funds, and by the true nobility of his character, which has lent distinction to its proceedings during an eventful period of its history."

Merck's "Digest."—We have received No. 1 of this new periodical, which is to consist of a selection of reports on new chemicals and drugs, taken from the latest medical, pharmaceutical, and other scientific literature. The first number is devoted to the description of the glycerino- or glycerophosphates and their applications. Glycerophosphoric acid, $H_2PO_4C_3H_5(OH)_2$+aq., is a pale yellow, oily, odourless liquid, having a sour taste; it is soluble in water and alcohol; its natural source is a decomposition product formed during digestion. Lecethin, the chief phosphorus constituent of food, is decomposed in its passage through the system into choline and glycerophosphoric acid; the latter is the form in which phosphorus is assimilated. The acid is not used medicinally by itself, but in the form of salts of ammonium, calcium, iron, potassium, quinine, &c. Physiologically phosphoglyceric acid possesses an elective action upon the nutrition of the nerves, and is said to be beneficial in cases of sciatica, neurasthenia, convalescence from influenza, and acute febrile affections, &c. It may be administered either internally or as a subcutaneous injection.

The Theory of Incandescent Gas-Lighting.—M. Drossbach.—According to the author the light given by an Auer mantle is due to the influence exercised by the molecule of oxide of cerium. This influence consists in bringing the calorific vibrations of the thorina into harmony with the calorific waves of the flame, which are then transformed into luminous waves. The author has prepared nitrates of thorium and cerium as pure as possible, and he found that the maximum illuminating power was given by a mantle containing 99·1 per cent of oxide of thorium, and 0·9 per cent of oxide of cerium. The substitution of zirconium for thorium gives bad results. He concludes that oxide of cerium does not possess any chemical or catalytic action. It has been stated that thorina prepared from the nitrate is always very voluminous, and that the great surface it offers to the flame favours the catalytic action of the oxide of cerium. Now the author shows that the sulphate, which makes a compact oxide, gives as good results as the nitrate.—*Journ. für Gasbeleuchtung*, xli., p. 352.

MEETINGS FOR THE WEEK.

TUESDAY, 14th.—Royal Institution, 3. "The Morphology of the Mollusca," by Prof. E. Ray Lankester, M.A., LL.D.

WEDNESDAY, 15th.—Society of Arts, 8. "The Balloon as an Instrument of Scientific Research," by the Rev. J. M. Bacon, F.R.A.S.

—— Institution of Mining and Metallurgy, 8. "Notes on Dry Crushing on the Witwatersrand," by F. White. "Notes on Economical Mining at Myall's United Gold Mine, New South Wales," by W. R. Thomas. "Mica Mining in Bengal, India," by A. M. Smith.

—— Microscopical, 7.30. Exhibition of Objects shown by Multiple Colour-illumination, by J. Rheinberg.

THURSDAY, 16th.—Royal Institution, 3. "Toxins and Antitoxins," by Dr. Allan Macfadyen, M.R.C.S.

—— Chemical, 8. "On the Absorption-spectrum and Constitution attributed to Cyanuric Acid," by W. N. Hartley, F.R.S. Ballot for the Election of Fellows.

FRIDAY, 17th.—Royal Institution, 9. "George the Third as a Collector," by R. R. Holmes, M.V.O., F.S.A.

SATURDAY, 18th.—Royal Institution, 3. "The Mechanical Properties of Bodies," by The Right Hon. Lord Rayleigh, F.R.S., &c.

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THE CHEMICAL NEWS.

Vol. LXXIX., No. 2047.

APPLICATION OF LIQUID HYDROGEN TO THE PRODUCTION OF HIGH VACUA, TOGETHER WITH THEIR SPECTROSCOPIC EXAMINATION.*

By JAMES DEWAR, M.A., LL.D., F.R.S.

As an illustration of the extraordinary power of the new cooling agent—liquid hydrogen,—the extreme rapidity with which high vacua can be produced by its use is perhaps one of the most striking. The absolute boiling-points of hydrogen, oxygen, and chlorine are respectively 35°, 90°, and 240°; in other words, oxygen boils at a temperature two and a half times higher than liquid hydrogen, and liquid chlorine similarly two and a half times that of liquid oxygen. From this we infer that liquid hydrogen as a cooling agent ought to be relative to liquid air as effective as the latter is compared to that of liquid chlorine. Now chlorine at the temperature of boiling oxygen is a hard solid, some 80° below its melting-point, and in this condition has an excessively feeble vapour pressure. When liquid hydrogen freezes air out of a sealed tube by immersing the end in the liquid, it is to be inferred that no measurable pressure of air ought to be left in the vessel. If we apply Van der Waal's law of corresponding temperatures to the case of hydrogen, the above inference is made unimpeachable. An approach to some knowledge of what the tension of air must be about the boiling-point of hydrogen can be attained by exterpolating the vapour-pressure curves of oxygen and nitrogen. Taking the following range of boiling-point temperatures for nitrogen and oxygen, viz., from the critical-point to the boiling-point under diminished pressure, two Willard Gibbs formulæ were calculated, with the following results :—

Nitrogen	Temp. abs.	127°	78·6°	59°
	Pressure in m.m..	25,900	740	26

Nitrogen. $\log_{10}p = 11{\cdot}5561 - \frac{400{\cdot}02}{T} - 1{\cdot}8980 \log_{10}T$ . . 1.

Oxygen	Temp. abs... ..	154°	90·3°	61·3°
	Pressure in m.m..	37,592	740	7·5

Oxygen. $\log_{10}p = 9{\cdot}4699 - \frac{422{\cdot}22}{T} - 0{\cdot}9843 \log_{10}T$ . . 2.

Another Gibbs formula was calculated, taking Estreicher's values for the vapour-pressure of liquid oxygen below its boiling-point, viz. :—

Temp. abs.	91·44°	78·1°	62·8°
Pressure in m.m..	743·8	141·8	7·5

Oxygen. $\log_{10}p = 16{\cdot}0670 - \frac{524{\cdot}72}{T} - 3{\cdot}8024 \log_{10}T$ . . 3.

We deduce from these formulæ the following vapour-pressures at the temperature of boiling hydrogen :—

1. Nitrogen..	0·0015	Pressure in m.m., 35° abs.
2. Oxygen ..	0·000076	do.
3. ,, ..	0·000016	do.

The results of calculation, taking the formulæ for the widest range of pressures, viz., 1 and 2, may probably be the surest, but in any case those values must be taken as a *maximum*, seeing they refer to the liquid state, while both oxygen and nitrogen at the temperature of 35° absolute, are hard solids, and must therefore have dropped to lower tensions than that of the exterpolated liquid vapour-pressure curves. It is curious to note that at this low temperature the theoretical ratio of the tensions of nitrogen and oxygen is as 20 to 1. Direct measurements of

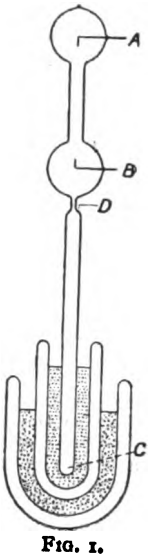

Fig. 1.

Fig. 2.

the vapour pressure of nitrogen at the melting-point, or 60° absolute, gave the value of 26 m.m., and a ratio of the tensions of nitrogen to oxygen of 6 to 1, whereas from the curves the value ought to be 6·7 to 1. Olszewski gives

Fig. 3.

the tension of nitrogen at −214° as 60 m.m., and as at this temperature the oxygen tension is 3·8 m.m., the ratio of the saturated pressures of the two gases at the melting-point of nitrogen would be as 16 to 1, which is far too high. Probably the oxygen value will be nearest the

* A Paper read before the Royal Society, December 15, 1898.

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truth, seeing it has the lowest melting-point. The tension is about a ten-millionth of an atmosphere. In the case of nitrogen, the maximum theoretical pressure would be one five-hundred-thousandth of an atmosphere. It is safe to infer that the vacuum left after liquefying the air out of a vessel by means of liquid hydrogen cannot exceed the millionth part of the atmospheric pressure, exclusive of the pressure resulting from any incondensable material other than nitrogen and oxygen. This is just about the pressure of the vapour of mercury at the ordinary temperature in the Torricellian vacuum, so that as good an exhaustion ought to result as can be got by boiling out a space with mercury. There is another way in which the question may be put. Assuming the molecular latent heats are approximately proportional to the absolute boiling-points, then we can, from a comparison with the oxygen value, deduce that of hydrogen, and thereby get the constants in a two term formula for the vapour-pressures. For pressures below an atmosphere, the following approximate formulæ were deduced:—

$$\text{Oxygen} \ldots \log p = 7{\cdot}2058 - \frac{392{\cdot}6}{T} \text{ m.m.} \quad . \quad . \quad . \quad 4.$$

$$\text{Hydrogen} \quad \log p = 7{\cdot}2428 - \frac{152{\cdot}7}{T} \text{ m.m.} \quad . \quad . \quad . \quad 5.$$

From these expressions it follows that at its boiling-point, or 35° absolute, hydrogen has 7/852000 times the pressure of oxygen, or the latter pressure is about the eight-millionth of an atmosphere. A similar formula, calculated from the critical- and boiling-point data, gives substantially the same order of quantities. Formula 4 for oxygen tensions must be fairly accurate, seeing it gives a theoretical latent heat of about 56 units per grm. of liquid evaporating at the boiling-point, whereas direct determinations result in 55 units. To test this inference, the following plan of experimenting was adopted:—Ordinary shaped vacuum tubes, like A, B, used for the spectroscopic examination of gases, with and without electrodes (Figs. 1 and 2), having a capacity ranging from 15 to 25 c.c., had pieces of quill tubing about a foot long sealed on. The tubes were contracted at D to about 1 m.m., so that they could be sealed off with rapidity. The end C sometimes terminated in a small bulb (Fig. 3), in order to give increased cooling surface, and, when necessary, to allow many times the volume of air in A B to enter and be condensed with the object of accumulating any incondensable residuum.

The tubes were filled with air, oxygen, and nitrogen at the atmospheric pressure. The liquid hydrogen collected in the vacuum vessel, immersed in another similar vessel full of liquid air, being ready, the end C was dipped in the liquid for a little over a minute, and the tube A B sealed off at D, so that on removal from the hydrogen bath the solid air might melt and distil off wihout generating any pressure. On attempting to pass the spark through vacuum tubes prepared in this manner, their excellent exhaustion was revealed by great resistance to the passage of the discharge, and the high phosphorescence of the glass. Two tubes, kindly prepared by Sir William Crookes with platinum electrodes that he had previously sparked to remove gases and impurities on the glass before filling with dry air, gave, when treated in the manner described, such high vacua that the tubes had to be heated in order to get any spark to pass. Thus, it is proved that the tension of solid nitrogen and oxygen at the temperature of boiling hydrogen is below the millionth of an atmosphere, seeing there is less difficulty in getting a discharge to pass in tubes exhausted to this extent. In order to get some definite idea of the limit of the exhaustion produced, two tubes, such as have been described as suitable for the liquid hydrogen experiments, might be joined together and filled with oxygen or nitrogen at atmospheric pressure, and simultaneously exhausted with the mercurial pump to a small fraction of an atmosphere, and then sealed off from the pump and each other. One of these two identical tubes could then be subjected to the hydrogen cooling, following the directions already given, and the two vacuum tubes now compared. If there was a marked difference in resistance to the passage of the discharge in the frozen tube, then something must have condensed, and by a few tentative trials a limit might be reached when the initial exhaustion was unaffected by the hydrogen cooling. Such experiments have not yet been made. The presence of any vapour of mercury would require to be carefully eliminated, otherwise the method would not be satisfactory. Tubes that are prepared without taking special precautions to exclude organic matter and water from the glass, deteriorate, especially with electrodeless tubes after the discharge has taken place for some time.

The rapidity with which the vacua are attained is such as theory would suggest, assuming a hole of a square millimetre in section through which the air rushes into the condenser and that a velocity of current between 600 and 700 feet a second is attained, then a vessel of 20 c.c. capacity could be reduced in pressure in one second to 1/10 of the initial pressure, and if the same rate is continued at the end of sixty seconds to $(\frac{1}{10})^{60}$. Sir George Stokes has been good enough to consider the problem, and writes as follows:—

"Let V be the volume of the vessel, A the area of an aperture by which the air is conceived as rushing out with the velocity v, ρ the density of the air in the vessel at the time t, D the initial density—that is, the atmospheric density.

"Then, according to our hypothesis, $Av.dt$ is the volume of air, and, therefore, $Av\rho.dt$, the mass of air, which rushes out in the time dt. But this equals the loss of mass of air in the vessel during the time dt, and, therefore,—

$$Av\rho \,.\, dt = -V d\rho,$$

a differential equation of which the integral is—

$$\rho = De^{-Avt/V}.$$

"Suppose now V to be 20 c.c., or 20,000 c.m.m., A to be the area of a circle of 1 or 2 m.m. diameter—say 2 sq. m.m., v to be 333 m., or 333,000 m.m., t (in seconds) to be 60; then—

$$\log_e \frac{D}{\rho} = \frac{2 \times 333{,}000 \times 60}{20{,}000} = 1998,$$

$$\frac{D}{\rho} = 5254 \times 10^{434}.$$

"This would give a density of almost inconceivable smallness. Doubtless the supposition made above as to the rate of discharge is very wide of the mark, being much too great. If the velocity of rushing is about half the velocity of sound, the ratio of densities would become 72×10^{217}. If so, it is satisfactory to find that the mathematical following out of the hypothesis leads to a density of the residual air in the vessel which is enormously below what suffices to account for the observed result." A practical mode of rapidly attaining a high vacuum in any vessel is to displace the air with carbonic or sulphurous acid, either at the atmospheric or under diminished pressure, and then to freeze out the remaining gas by the use of liquid air, just as in the experiments with liquid hydrogen.

The first vacuum tube was an electrodeless one, the air had not been dried, nor the glass specially cleaned. On spectroscopic examination it showed hydrogen lines bright along with the second or compound line spectrum of the same gas, and a series of bright bands defined on the less refrangible side, diffuse on the more refrangible, which occur in the yellow, green, blue, and indigo. These bands were found to be identical with the carbonic oxide spectrum. With a Leyden jar in the secondary circuit the line spectrum of hydrogen disappeared, leaving the second spectrum fainter; but the carbonic oxide bands remained bright, and there was no appearance of the hydrocarbon

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spectrum. The second tube had aluminium electrodes, and, like the last, had no special treatment in filling in the air. This tube showed also the line spectrum and the second spectrum of hydrogen; the latter being bright along with the carbonic oxide spectrum; but on sparking the latter disappeared. No appearance of the hydrocarbon spectrum could be detected, but there was a suspicion of bands in the indigo like the negative pole spectrum of nitrogen. The addition of a Leyden jar brought out nothing new, only intensifying the line spectrum of hydrogen, while leaving the second spectrum bright. In neither of the above tubes could any lines of nitrogen or oxygen be recognised. The third tube was filled with air drawn over cotton-wool, red-hot copper oxide, and phosphoric pentoxide, no rubber joints being employed. The spectrum showed the carbonic oxide bands and the hydrogen line spectrum as before. Only the second hydrogen spectrum was feeble. There was a yellow line, W. L. 5849, identical with one occurring in the natural gas from the King's Well at Bath. In a paper on "The Liquefaction of Air and the Detection of Impurities" (*Chem. Soc. Proc.*, November, 1897), the separation of helium from this gas is described by liquefaction and fractionation, and it was observed that during the sparking the helium lines were well marked along with "*others, the origin of which must be settled later.*" It was further observed, "*With a modified form of apparatus it will be possible to collect any residuary gas from the use not of 3 cubic feet of air or Bath gas, but from hundreds of cubic feet of such products.*" The helium and other associated material was shown to be more volatile than nitrogen. Pursuing this course of investigation in the summer of this year, the volatile portion of air was examined, when the presence of material giving the same lines as Bath helium was recognised. While this investigation was in progress, Professor Ramsay and Dr. Travers observed the same spectrum in the more volatile portion of argon which they have associated with a new element called neon. The use of liquid hydrogen, as described, proves that the most characteristic line of neon in the yellow, about W. L. 5849, can be detected in 25 c.c. of ordinary air, and the presence of helium in the atmosphere is confirmed.*

A fourth tube, filled like the preceding one, had a phosphoric pentoxide tube left on. This showed again the carbonic oxide bands, but no hydrogen lines could be detected; while the oxide of copper ought to have removed all free hydrogen and transformed all the organic matter into carbonic acid and water. Yet it appears that the spectrum of the carbon compounds is difficult to remove from electrodeless tubes, probably owing to carbonic acid coming from the glass. There were some broad diffuse bands that may arise from the drying agent. The absence of hydrogen in this tube suggests that its presence in the third tube was due to vapour of water coming slowly from the glass. I am greatly indebted to Professor Liveing for making a careful examination of the spectra of these tubes.

Sir William Crookes was good enough to prepare two tubes with platinum electrodes, which he sparked in vacua till all hydrogen disappeared, and then filled with dry air, but without the use of red-hot copper oxide or any agent for the absorption of carbonic acid or the destruction of organic matter. After the cooling with liquid hydrogen, he found on spectroscopic examination, in one no hydrogen, but two faint lines, one about 5852 W.L. and the other 5676 W.L. The second tube showed the same yellow about 5852, the helium line along with 5939 and 6145, the hydrogen lines C and F, and some red lines. The observations of Crookes confirm the presence of neon, helium, and hydrogen. The absence in his tubes of the carbonic oxide spectrum is important, seeing all the electrodeless tubes gave this spectrum. In these tubes the vacuum was very high, and it was difficult to observe the gaseous spectrum. Still, the fact of finding hydrogen in one and not in the other leaves the presence of free hydrogen in the atmosphere as a question for further inquiry. The tube that did not contain hydrogen was heated very hot in order to get a discharge, and then the spectrum showed some bands like the negative glow of nitrogen. Occasionally a jar discharge was got to pass, and when this took place the nitrogen lines could be seen. An electrodeless tube filled carefully with oxygen made from fused chlorate of potash, which was contained in an extension of the vacuum tube, gave nothing but the carbonic oxide bands. In future experiments it will be easy to concentrate all the least volatile material in air or other gases, and thereby to make a more thorough examination of the spectrum. In the meantime my object is to show one of the scientific uses of liquid hydrogen.

I have to thank Mr. Robert Lennox for efficient aid in the conduct of the difficult experiments. Mr. Heath has also helped in the work.

* In a paper along with Professor Liveing, "On the Spectrum of the Electric Discharge in Liquid Oxygen, Air, and Nitrogen" (*Phil. Mag.*, 1894), we noted that during the distillation and concentration *in vacuo* of liquid oxygen and air under diminished pressure that two bright lines appeared in the spectrum at wave-length 557 and 555, and that one of these lines was very near the position of the auronal line. These lines are now attributed by the same chemists to a new element, crypton.

DISPLACEMENT OF METALS BY MAGNESIUM.

By EDWARD G. BRYANT, B.Sc.

It is stated in many text-books that magnesium will replace zinc, silver, lead, and copper, if added to solutions of the salts. This is quite true; but when exercises are set to students to determine the equivalents of these metals by means of magnesium, failure occurs, because in every case secondary actions are set up which result in the change of part of the magnesium or the other metal into oxides or basic compounds.

Clowes and Caven (*Journ. Chem. Soc.*, 1898) have shown this in the case of copper and magnesium. The following experiments were undertaken with the view of examining the action on the other metals mentioned above. The materials used were not *specially* purified; the experiments were made under the same conditions that laboratory students would have to work under.

1. *Magnesium and Zinc Sulphate.*—The following table shows that in every case, whether the solution be hot or cold, strong or weak, only a little more than 50 per cent of metallic zinc can be obtained. The first three results are certainly too high, and are due to all the magnesium not having disappeared. In the cold the action takes several days to complete, as judged by the gradual increase in the amount of gas generated. The residue always consisted of greyish metallic zinc and a considerable quantity of zinc and magnesium oxides. There was no sulphate present in the residue, and it had no effect on permanganate of potash. The amount of metallic zinc was estimated by measuring the hydrogen given off on dissolving the residue in dilute HCl. The gas given off during the reaction could be used as a check, as it measured the amount of oxidation of the two metals. Magnesium ribbon was used.

	Concentration of $ZnSO_4$.	Temperature.	Zinc reduced. Per cent.	
1.	5 per cent	13° C.	63	These are probably several per cent too high.
2.	10 „	13	66	
3.	10 „	60	65	
4.	20 „	70—80	55	
5.	5 „	13	60	
6.	2 „	5	56·8	
7.	20 „	13	54	

2. *Magnesium and Lead.*—Kirn (Chem. News, xxxii., 309) states that magnesium in lead nitrate is quickly covered with metallic lead, the lead soon changing into hydrate. I found that whether I used lead nitrate,

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chloride (in hot solution), or acetate, and whether the solution was made slightly alkaline or not, that hydrogen was given off as well as lead reduced. In the case of lead chloride, the lead appeared as brilliant flakes, otherwise as a black powder.

As the gas came off very slowly at first, but increased when the solution was heated or after a certain amount of lead was deposited, the experiment was varied by dropping the solution on to the magnesium contained in a filter, just fast enough to keep the funnel about half full. No gas could be seen under these conditions, but after four hours there was still metallic magnesium left coated with lead, and only 50 per cent of the theoretical quantity of lead was obtained. I did not find that the lead oxidised under these conditions as long as it was covered with liquid; but when being dried it became perfectly white, and was estimated as PbO after ignition. The amount of magnesium used was from 20 to 50 m.grms. in fine powder.

3. *Magnesium and Silver.*—The action is very similar to that of lead, no gas being evolved at first, but the amount increasing as the experiment progresses or on heating. If any of the magnesium powder floats on the surface, a brilliant mirror of silver forms round it. The silver comes down in black flocculent masses, but on standing or washing with dilute acid turns to brownish crystalline particles. The table gives the results obtained; once the theoretical result occurred. From 20 to 50 m.grms. magnesium used.

Concentration of $AgNO_3$.	Temperature.	Amount of silver recovered. Per cent.	Remarks.
2 per cent	15° C.	66	Ribbon used, free Mg left in residue.
2 ,,	60	50	MgO in residue.
2 ,,	15	66	Ribbon; much metallic Mg in residue.
2 ,,	13	65	Result taken after two days; no free Mg, but much MgO in residue.
2 ,,	15	102	$AgNO_3$ dropped on Mg filings for 2 hrs. No gas evolved.
2 ,,	15	65 (twice)	Rather coarser filings than the last. No visible gas evolved.
2 ,,	15	112·2	Solution of $AgNO_3$ dropped for 4 hours on fine filings. No gas evolved.

I have never been able to account for the last result. There is a certain accordance about the others, which renders it probable that the theoretical result, or near it, might be obtained if sufficient precautions are used, but it cannot be described as an elementary exercise.

King's School, Pontefract,
February 4, 1899.

THE ACTION OF THE BACILLUS COLI AND EBERTH'S BACILLUS ON NITRATES.

By L. GRIMBERT.

I HAVE already shown that, contrary to the opinion of certain writers, the bacillus coli and Eberth's bacillus do not give off nitrogen when cultivated in a 1 per cent solution of nitrated peptone; but as, on the other hand, we get a disengagement of gas when the solution of peptone is replaced by a peptonised beef broth, it appeared to me to be interesting to try and find the cause of this different action, and to discover the origin of the nitrogen produced.

I therefore undertook a number of experiments in which I estimated the amount of gas given off, the nitrate destroyed, the nitrite remaining, and what I have termed the *amidised nitrogen*, that is to say the nitrogen furnished by the complex amidised materials in my culture media, before the intervention of any microbes, but when treated only by hypobromite of soda.

A. With the object of emphasizing the difference which exists between the action of bacilli on the nitrates and that of true denitrifying agents, I infected, on the one hand, a peptonised broth nitrate to 1 per cent with the bacillus coli and with Eberth's bacillus, and, on the other hand, a solution of nitrated peptone with the pyocyanic bacillus.

At the end of a month I obtained the following results:—

The pyocyanic bacillus gave off nitrogen only. The volume of nitrogen collected (100·48 c.c.) is equal to the nitrate destroyed (100·41 c.c.), and is seven or eight times greater than that of the amidised nitrogen (13·80 c.c.). The colon and typhoid bacilli give off nitrogen and carbonic acid. The volume of this nitrogen (28·09 c.c. and 26·96 c.c.) is practically the double of that which corresponds to the nitrate destroyed (12·34 c.c. and 13·0 c.c.), and much less than that of the amidised nitrogen from the culture (47·12 c.c.). Only one-half of the nitrogen is therefore furnished by the nitrate, the other half coming apparently from the amidised materials of the culture medium, on account of the reaction which takes place between these principles and the nitrous acid produced by the bacteria. This is the secondary phenomenon of a long known biological fact, viz., the reduction of nitrates by the bacilli of Eberth and Escherich.

B. If to a nitrated solution of peptone we add substances capable of losing their nitrogen by the action of nitrous acid, we ought to have a disengagement of gas; this is what takes place with extract of meat rich in waste nitrogenous matter, but only slightly nutrient in itself. The bacillus coli sown in a solution of peptone nitrated to 1 per cent does not give off any nitrogen. In a nitrated solution of meat extract without peptone it gave 7 c.c. at the end of a month, a volume corresponding to double that of the nitrate destroyed (2·9 c.c.), and in a 1 per cent solution of peptone, to which is added 1 per cent of meat extract and 1 per cent of potassic nitrate, we obtain, under the same conditions, 23·45 c.c. of nitrogen, the nitrogen corresponding to that which has disappeared being only 6·95 c.c.

C. With a 1 per cent solution of peptone giving 13·8 c.c. of amidised nitrogen, we can thus, by increasing the proportion of peptone, introduce into the solution an amount of amidised principles sufficient to cause a further disengagement of nitrogen. In fact, a 5 per cent solution of peptone containing 1 per cent of nitrate of potassium, and representing 71 c.c. of amidised nitrogen, gives, with the bacillus coli, 16·29 c.c. of nitrogen, and with Eberth's bacillus 11·29 c.c.; the amounts of nitrogen lost by the nitrate being respectively 8·7 c.c. and 2·9 c.c.

D. Contrary to certain opinions, the presence of nitrites does not stop the fermentation. The two bacilli develope very well in a peptonised solution of extract of meat containing 1 per cent of nitrite of potassium, and nitrogen is given off in a quantity equal to or even greater than that which they gave in the same medium when nitrated.

To sum up, whenever the bacillus coli or the bacillus of Eberth have caused a disengagement of gas in a nitrated medium, the volume of nitrogen collected has always been at least *double* that which corresponds to the nitrate destroyed. Consequently *the nitrogen given off does not come exclusively from the nitrates.*

The denitrifying action of these bacilli is correlative with the presence of amidised materials in the culture medium. It seems to be the result of the secondary action exercised on these latter by the *nitrous acid* produced by the bacteria.

Nitrites do not interfere with the action of these bacilli.—*Journ. de Pharm. et de Chim.*, Series 6, vol. ix., No. 2.

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ON BECQUEREL'S RAYS AND POLONIUM.

By Madame S. CURIE.

THE discovery of Becquerel's rays is due to the researches undertaken after the well-known discovery by Röntgen of the photographic effects of certain phosphorescent and fluorescent substances. These researches appear to throw a new light on a part of physical science. We now propose to discuss certain new facts and ideas that these facts give rise to in respect to natural philosophy.

Uranic Rays.

In an article by M. Poincaré which appeared recently in the *Revue Générale des Sciences*, the following remark appeared:—"The glass of a Crookes tube when bombarded by the cathode rays becomes fluorescent; this fluorescence is associated with the emission of Röntgen rays. We may, therefore, reasonably enquire if all bodies, of which the fluorescence is sufficiently intense, do not emit Röntgen rays as well as luminous rays, no matter what may be the cause of the fluorescence."*

Shortly afterwards M. Henry showed that phosphorescent sulphide of zinc could produce photographic impressions through a sheet of black paper quite impervious to light.

Niewenglowski observed the same phenomenon with sulphide of calcium which had been exposed to light. These observations may be better understood by admitting that the photographic effect was due to invisible rays, analogous to X-rays, that were emitted by the bodies in question.

Later on M. Troost obtained strong photographic impressions with an artificial phosphorescent hexagonal blende through black paper and thick cardboard.

M. Becquerel made similar experiments with uranium salts, some of which are fluorescent. He obtained photographic impressions through black paper with the double sulphate of uranium and potassium. He first thought that this salt, which is fluorescent, behaves like the sulphides of zinc and calcium, but further observations showed that this analogy did not really exist. It is true that uranium salts act on photographic plates through opaque bodies, but this action is in no way connected with fluorescence. Uranium and all its compounds, whether fluorescent or not, act in the same manner, and metallic uranium is the most active of them all. M. Becquerel also noticed that light is not necessary, but that uranium compounds kept in the dark for years continued to act on photographic plates. This was an entirely new phenomenon. He also showed that uranic rays were possessed of the following properties:—They traverse opaque bodies, but are absorbed more easily, and are therefore less penetrating than Röntgen rays. They make the air through which they pass a conductor of electricity, as do Röntgen rays; this is an important property of both kinds of rays.

Thoric Rays.

Following these results it was only natural to ask if uranium was the only metal possessed of this property, and M. Schmidt has found that compounds of thorium are the only ones endowed with similar properties. The activity of the oxides of these two metals is equal, and, approximately, their compounds are more active in proportion to the amount of the metal they contain.

Uranic rays have been frequently called *Becquerel rays*; this name may be generalised by applying it also to thoric rays, and all rays of that character. I propose, however, the name *radioactive* to describe this phenomenon; *hyperphosphorescence*, which has been proposed, seems to me to give a false idea of its nature.

Polonium.

A certain number of minerals have been examined in a special apparatus designed for the purpose of measuring the conductivity of the air when under the influence of the rays emitted by radioactive substances; among these, pitchblende, chalcolite, autunite, clèveite, monazite, orangite, thorite, &c., were found to be radioactive. All these minerals contained either uranium or thorium, but in some cases the intensity of the action was quite unexpected; thus some pitchblendes were three times as active as metallic uranium; chalcolite (crystallised phosphate of uranium and copper) is twice as active as uranium; autunite (phosphate of uranium and lime) is just as active as uranium. This is in direct contradiction to the results obtained with *pure* uranium compounds which are less active than uranium itself. It therefore seemed probable that the above-mentioned minerals contained a small quantity of a very strongly radioactive body, different to uranium and thorium.

By experimenting it was first noticed that on subliming pitchblende in vacuo an extremely active body was obtained, more than thirty times as active as uranium, but there was very little of it. Eventually, by chemical means, a body was obtained having a radioactivity about 400 times greater than that of uranium. We imagine this to be a new element allied to bismuth, and we propose to call it *polonium*.

The acid solution of pitchblende was treated with sulphuretted hydrogen. The uranium and thorium remain in solution, but the precipitated sulphides are much more active than the original pitchblende. These sulphides contain lead, copper, bismuth, arsenic, and antimony. The active substance contained in the sulphides is insoluble in sulphide of ammonium; this separates it from the arsenic and antimony. The sulphides insoluble in sulphide of ammonium were dissolved in nitric acid; the active substance can be partially separated by sulphuric acid. By exhausting the sulphate of lead with dilute boiling sulphuric acid, a large part of the active substance carried down with the sulphate of lead can be dissolved. This new body which is in solution with the bismuth and copper is completely precipitated by an excess of ammonia; this separates it from the copper. Its separation from bismuth, which now alone remains, is not easy by the wet way; we can, however, obtain an approximate separation by fractional precipitation. For this purpose water is added to the hydrochloric or nitric solution; the portions first precipitated are by far the most active. To obtain a complete separation we must have recourse to sublimation of the sulphides in vacuo at about 700° C. The active sulphides are deposited in the form of a black layer in that portion of the tube which is about 250—300°. The sulphides of bismuth and lead remain in the hotter part of the tube.

The radioactive power of polonium is so great that it seems reasonable to enquire whether uranium and thorium do not owe their activity to the presence of a small quantity of this body. This did not appear probable, for if such was the case different samples of uranium compounds would have very different radioactivities, but in the course of a number of experiments made with various samples of metallic uranium, as well as with oxides and salts from various sources, I have never found any marked difference between the relative activities of the same compound.

Photographic Impressions. Fluorescent Effects Produced by Becquerel Rays.

Uranic, thoric, and polonic rays act on sensitive plates, the rays of thorium being less active than those of uranium.

Uranium compounds give a photographic impression after one hour. The substance we call sulphide of polonium gives a good impression after only three minutes, and there is a decided action noticed after even half a minute.

Uranium and the compounds of thorium have no apparent fluorescent action on platinocyanide of barium,

* At this time (January, 1896), the emission of X-rays, unaccompanied by fluorescence, as in the case of platinum anticathodes, was not yet known.

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but sulphide of polonium has a very distinct action. The experiment can be performed in the following manner:—The active substance is spread in a very thin layer over a portion of the surface of a metallic disc, the whole of the disc is covered with a very thin sheet of aluminium of the same diameter. The whole surface of the aluminium is then covered with a thin layer of platinocyanide of barium. On examining this in the dark, a faintly luminous area is noticed on the upper disc, and it is easy to make certain that this area is opposite the active substance. The rays emitted by this latter body have traversed the aluminium and excited the fluorescence of the platinocyanide above it, while the remainder of the disc remains dark. It thus appears that we can obtain an indefinite amount of light without the expenditure of any energy. A similar experiment with the oxides of uranium and thorium was not successful.

Conductivity of Gas under the Influence of Becquerel Rays.

To obtain simple theoretical conditions it is advisable to use plates the surfaces of which are great with regard to their distance apart. By varying the difference of potential between the plates, the strength of the field may be varied. In weak fields the intensity of the current is proportional to the strength of the field; a constant initial conductivity exists. As the field becomes stronger, the current increases less and less quickly, and tends—in the case of very strong fields—towards a practically constant limit.

The intensity of the current increases with the volume of air comprised between the plates; however, as the distance between the plates increases, the fresh layers of air introduced have less and less effect, as if the uranic rays were strongly absorbed by the air they traverse. Not only air, but oxygen, hydrogen, and carbonic acid gas are made conductors by the action of Becquerel rays. The experiments were carried out at the ordinary pressure, but others under variable pressures have also been tried, with the result that for pressures which are not too feeble the current is proportional to the pressure, at least in the cases of air and hydrogen.

The laws of the conductivity of air under the influence of Becquerel rays are analogous to those obtained with X rays. From this point of view we may imagine that gases submitted to the influence of Becquerel rays are partly *ionised*, and that it is the movement of the ions charged with electricity along the lines of the electric field which constitutes the current.

The Absorption of Becquerel's Rays.

To measure the absorption of Becquerel rays by solid bodies, the active substance is covered over with a plate of the material under examination. By this means, the proportion of rays transmitted by a given screen can be determined, provided always that the screen is a sufficiently good conductor. A sheet of aluminium 0·001 m.m. in thickness will only allow a fraction of the rays to pass, equal to 0·2 for uranium and 0·4 for oxide of thorium in a layer 0·005 m.m. thick. If a layer of oxide of thorium 0·006 m.m. thick is used, the same sheet of aluminium will allow rays to pass equal to 0·7.

Experiments published with regard to the reflection and refraction of Becquerel rays are not very conclusive, but the observations made are not comparable with the reflection and refraction of luminous rays.

Analogies and Differences between Becquerel and other Rays.

Becquerel rays are characterised by the following properties:—

They render gases which they traverse conductors of electricity; they produce photographic impressions. These two properties do not in any way depend on the past or present action of light on the bodies emitting these rays. They traverse all substances, glass, paper, metals, and liquids, but are, as a rule, absorbed to a great extent. Their emission appears to be spontaneous; it is constant, and indicates the presence of certain elements in the active substance. Their emission is but slightly influenced by the physical state of the active substance, or by the presence of the small amounts of impurities they may contain. It is important to remember these points when endeavouring to establish analogies and differences between these and other kinds of rays which appear to resemble them.

The spontaneous emission of these rays appears to give rise to a continuous disengagement of energy of which we cannot find the source. This is in direct contradiction with Carnot's principle. While admitting that this giving off of energy exists, it is possible to conceive the production of the phenomenon in different manners. For instance, it may be a phosphorescence of very considerable duration caused by the action of light; but this hypothesis is hardly probable. It may be an emission of matter accompanied by a loss of weight of the radioactive bodies, or the utilisable energy may be constantly diminishing. Again, it may be a secondary emission provoked by rays analogous to X-rays (these being constantly in existence in space, much more penetrating than X-rays, and only commencing to be absorbed by elements of a high atomic weight, such as uranium and thorium). In this last hypothesis we have endeavoured to make the emission of these rays fit in with Carnot's principle, but the question may just as well be asked whether Becquerel rays may not be produced at the expense of the heat in the surrounding medium, contrary to this principle.

Since this research was made, M. and Mdme. Curie have quite recently, in conjunction with G. Bémont, discovered in pitchblende indications of an element (radium) allied to barium in its chemical properties, but differing in its radio-activity, and having a definite line in its spectrum, which is evidence of the existence of a true element (see *Comptes Rendus*, cxxvii., p. 1215; also Chemical News, lxxix., p. 1).—*Revue Générale des Sciences*, Jan. 30, 1899.

THE

SEPARATION OF COPPER AND ANTIMONY.

By M. LUCAS.

One of the most frequently used methods of effecting this separation is to precipitate the two metals in the form of sulphides, and to re-dissolve the sulphide of antimony in sulphide of sodium. Complete separation often requires four or five successive treatments; we can only check the progress of the reaction on very small portions of the liquid, so as not to affect the analysis; and further, there is always a small portion of sulphide of copper dissolved by the sulphide of sodium, and if the antimony is afterwards estimated by electrolysis, this copper will be deposited with it on the cathode.

It seemed to me to be more simple and more advantageous to proceed in the following manner:—After the first treatment with sulphide of sodium, the whole is treated with 5 c.c. of peroxide of hydrogen to destroy the polysulphides, and we then make a preliminary electrolysis following Classen's method, but without previously removing the sulphide of copper which collects at the bottom of the liquid.

The metallic deposit is then weighed, and the liquid heated to re-dissolve the precipitated sulphur, treat with 5 c.c. of peroxide of hydrogen to destroy the polysulphides, add a little sulphide of sodium, and electrolyse again; the second deposit covers the first; weigh these two together and keep the metal.

Do this a third time, but use a different cathode; weigh this third deposit, re-dissolve in nitric acid, and estimate

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ASTOR, LENOX AND TILDEN FOUNDATIONS.

Composition of the sample.		Amounts of Sb and Cu weighed.							
Pure Sb.	Pure Cu.	First electrolysis. 12 hours.	Second electrolysis. 6 hours.	Third electrolysis. 12 hours.	Fourth electrolysis. 6 hours.	Total Sb.	Cu from cathodes.	Electrolytic Cu.	Total Cu.
0·110	0·096	0·106	0·006	0·0083	0·004 Cu only.	0·110	0·0143	0·0817	0·093
0·0736	0·150	0·0682	0·0043	0·0053	0·0018 Cu only.	0·0739	0·0057	0·1443	0·150
0·100	0·100	0·103	0·0043	0·001 Cu only.	—	0·0995	0·0088	0·0912	0·100
0·107	0·032	0·1075	0·005	0·0025 Cu only.	—	0·1075	0·0075	0·0248	0·0323
0·100	0·100	0·101	0·005	0·004	0·002 Cu only.	0·099	0·013	0·0865	0·0995

the copper colorimetrically to see whether or no there is still a deposition of antimony, and if it is necessary to make a fourth electrolysis.

The deposit of copper and antimony is dissolved in nitric acid and filtered. Treat with ammonia and a few drops of sulphide of ammonium. The sulphide of copper which is precipitated is filtered, re-dissolved, and the copper estimated by colorimetry by means of ferrocyanide of potassium. This amount of copper is deducted from the weight of antimony, and added to that of the copper estimated in the residue. This secondary estimation of the copper is indispensable, no matter in what manner the sulphide of sodium has been used.

Finally, the sulphide of copper is filtered, but only after the major part of the sulphide of sodium has been destroyed by peroxide of hydrogen. I give some figures obtained by this method (see Table).

The fourth analysis was carried out in the presence of 0·098 grm. of pure tin, which was afterwards found by analysis.

This method is a more or less perfect application of the method of separating copper and iron electrically as done by M. Riche, and nickel and iron as done by M. O. Ducru.—*Bull. Soc. Chim.*, Series 3, vol. xix.-xx., No. 18-19.

PROCEEDINGS OF SOCIETIES.

CHEMICAL SOCIETY.

Ordinary Meeting, February 2nd, 1899.

Professor Dewar, F.R.S., President, in the Chair.

Mr. F. W. Dootson was formally admitted a Fellow of the Society.

Certificates were read for the first time in favour of Messrs. James Herbert Allworthy, Laxton School, Oundle; Peter Auchinachie, 12, Mid Street, Keith, N.B.; Kendall Colin Browning, St. John's College, Cambridge; William Collingridge, Port Sanitary Office, Greenwich, S.E; Archibald Glen Kidston Hunter, Dunedin, New Zealand; Lawrence Christopher Panting, 9, Beverley Road, Anerley, S.E.; Samuel Barnett Schryver, D.Sc., Ph.D., 27, Arundel Gardens, W.: Arthur John Shelton, 19, Sturry Street, Poplar, E.; Robert Tatlock Thomson, 156, Bath Street, Glasgow.

Of the following papers those marked * were read:—

*13. "*Maltodextrin, its Oxidation Products and Constitution.* By Horace T. Brown, LL.D., F.R.S., and J. H. Millar.

The subject of this paper is the maltodextrin which occurs amongst the intermediate products of starch hydrolysis with diastase, and to which the empirical formula—

$$\begin{cases} C_{12}H_{22}O_{11} \\ (C_{12}H_{20}O_{10})_2 \end{cases}$$

has hitherto been assigned (Brown and Morris, *Trans.*, 1885, xlvii., 527). Although present in considerable quantities in starch transformations which have been arrested at the right point, its preparation in a pure state, and in sufficient amount for extended work, is a very laborious process. When isolated, it was found to have properties corresponding to $[\alpha]_D$ 181—183, and R 42—43, and was completely hydrolysed to maltose by diastase, and to *d* glucose by acids.

When maltodextrin is carefully oxidised with mercuric oxide and barium hydroxide until its power of reducing Fehling's solution disappears, the greater part of the product is obtained as the barium salt of a definite and complex carboxylic acid, which is provisionally called *maltodextrinic acid A*. This has been isolated. Its properties correspond to $[\alpha]_D$ 192·3, R 0, and its calcium salt contains 2·4 per cent of calcium. Maltodextrinic acid A is hydrolysed both by diastase and by dilute acids. Under the action of diastase it yields 40 per cent of maltose, and 60 per cent of another carboxylic acid of less complexity: this is *maltodextrinic acid B*, the calcium salt of which contains 3·8 per cent of calcium.

When hydrolysed by dilute oxalic acid, maltodextrinic acid A yields 85·8 per cent of *d*-glucose, and another still simpler acid which is shown to be a C_5-derivative. Maltodextrinic acid B, when hydrolysed by oxalic acid, also yields this same C_5-acid and 67·7 per cent of glucose.

The final C_5-acid corresponds in composition to $C_5H_{10}O_6$, and appears to be a normal carboxylic acid derived from a pentose. Since this acid can now be prepared in fair quantities by the oxidation of maltose with mercuric oxide, the authors expect to be able very soon to put its exact nature beyond doubt. It has many properties in common with those of xylonic acid.

If the constitutional formula of maltose is taken as—

$$CH_2OH\cdot CHOH\cdot CH\cdot(CHOH)_2\cdot CH\cdot O\cdot CH_2\cdot(CHOH)_4\cdot CHO,$$

the polysaccharide maltodextrin may be regarded as being made up of three such molecules with the elimination of the elements of $2H_2O$. Written in an abbreviated form, the formulæ of maltodextrin and of maltodextrinic acid A may be expressed thus:—

$$O<\begin{matrix} C_{12}H_{21}O_{10} \\ C_{12}H_{20}O_9 \\ C_{12}H_{21}O_{10}< \end{matrix}$$

Maltodextrin.

$$O<\begin{matrix} C_{12}H_{21}O_{10} \\ C_{12}H_{20}O_9 \\ C_5H_9O_5 \end{matrix}$$

Maltodextrinic acid B.

the sign < being used to denote the open carbonyl.

The hydrolysis of maltodextrinic acid A in two successive steps by diastase and acids respectively may be represented in the following manner:—

1. *Diastase Hydrolysis.*

$$O<\begin{matrix} C_{12}H_{21}O_{10} \\ C_{12}H_{20}O_9 \\ O<C_5H_9O_5 \end{matrix} + H_2O = O<\begin{matrix} C_{12}H_{21}O_{10} \\ C_5H_9O_5 \end{matrix} + C_{12}H_{22}O_{11}$$

Maltodextrinic acid A. Maltodextrinic acid B. Maltose.

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2. *Acid Hydrolysis.*

$$O\begin{matrix}<C_{12}H_{21}O_{10}\\C_5H_9O_5\end{matrix} + 2H_2O = C_5H_{10}O_6 + 2C_6H_{12}O_6$$

Malodextrinic acid B. Pentose acid. Glucose.

In an appendix to the paper, the authors describe the standard methods they now employ to determine the amount of glucose which a carbohydrate or its derivative yields on complete hydrolysis with oxalic acid. The results of thus hydrolysing soluble starch, maltose, maltodextrin, and maltobionic acid are given.

*14. "*On Attempts to prepare Pure Starch Derivatives through their Nitrates.*" By Horace T. Brown, LL.D., F.R.S., and J. H. Millar.

This paper records the efforts made by the authors to obtain some of the hydrolytic products of starch in a pure state by preparing their nitric esters and regenerating them by treatment with ammonium sulphide.

Although perfectly successful as regards soluble starch, it was not found possible to regenerate from their nitrates substances like maltodextrin, amylodextrin, and the stable dextrin, the recovered product always showing signs of having undergone some oxidation during the nitration process. All the reducing starch products, *i.e.*, those with an open carbonyl group, yield on nitration and regeneration indeterminate mixtures containing carboxylic acids.

*15. "*The Stable Dextrin of Starch Transformations, and its relation to Maltodextrin and to Soluble Starch.*" By Horace T. Brown, LL.D., F.R.S., and J. H. Millar.

When starch is transformed by an active diastase, such as that derived from an air-dried malt, at temperatures below 60°, the reaction proceeds with great rapidity until a resting stage is reached corresponding to $[\alpha]_D$ 150, R 80, for the mixed products of change. At this stage these products consist of maltose, and a dextrin which, comparatively speaking, is very resistant to the further action of the hydrolytic agent. An account is given of the mode of separation, and the dextrin was obtained ultimately with optical and reducing properties corresponding to $[\alpha]_D$ 195—195·7, and R 5·7 to 5·9. This residual reducing power is a property inherent to the dextrin, and is not due to admixture with a second reducing substance. This was shown by oxidising the dextrin with mercuric oxide and baryta, a definite dextrinic acid being produced.

Dextrinic acid is a complex carboxylic acid with distinct but feeble acid properties. It forms a well-defined calcium salt, containing 0·31 per cent of calcium, and under the influence of acid hydrolysis yields *d*-glucose and a residual C_5-acid, which is shown to be identical with that obtained by the complete acid hydrolysis of the two maltodextrinic acids already described. The amount of glucose given by this hydrolysis has been determined.

Dextrinic acid and its salts, and also the dextrin from which it is derived, unlike maltodextrin and maltodextrinic acid A, are but very slowly hydrolysed by diastase. After many hours' treatment at 50—60° a certain limited amount of change takes place, the resulting products being maltose and glucose in about equal proportions. The glucose is not derived from previously formed maltose, since it is observed when a malt-extract absolutely devoid of any maltose-hydrolysing power is employed.

The available evidence all points to the conclusion that the stable dextrin and the derivative polysaccharide acid, dextrinic acid, are built up of C_6-, and not, as in the case of maltodextrin, of C_{12}-groups. The dextrin molecule may be empirically regarded as made up of 39 $C_6H_{10}O_5$ groups in combination with a terminal $C_6H_{12}O_6$ group; or, more correctly, as a condensation of 40 glucose molecules, with the elimination of $39H_2O$. All the known properties of these substances agree with the view that their constitution may be expressed by the formulæ—

$$O_{39}\begin{cases}C_6H_{11}O_5\\(C_6H_{10}O_4)_{38}\\C_6H_{11}O_5<\end{cases} \qquad O_{39}\begin{cases}C_6H_{11}O_5\\(C_6H_{10}O_4)_{38}\\C_5H_9O_5\end{cases}$$

Stable dextrin. Dextrinic acid.

The paper concludes with a discussion of the constitution of the starch molecule in the light of this new work.

Discussion.

Dr. Armstrong expressed the opinion that the formulæ suggested by the authors conveyed an idea of instability scarcely in accordance with the behaviour of the compounds in question. He could not help thinking that their structure was such that the ordinarily active groups were in some way shielded from attack or rendered unapproachable. Obviously, however, much more had to be learnt on such subjects. The complexity of the starch molecule was altogether remarkable when it was seen that in plants the formation of starch took place with extraordinary facility, and apparently under very simple conditions: thus starch could be detected in *Spirogyra*, originally depleted of the carbohydrate, after a very few minutes' exposure to light. It was most important to obtain further information on such a matter, as well as on the structure of the starch molecule; he was glad, therefore, that Dr. Brown was also studying the problem from the biological side.

Mr. C. F. Cross remarked that the production of a C_5-hydroxy-acid under the conditions of the authors' experiments would add another and comparatively simple transition from hexose to pentosé derivatives, and further generalise the tendency to form C_5-products—of which lævulinic acid and furfural are typical examples, but contrasted with the present case by complete elimination of alcoholic OH-groups. It would be important to determine whether a C_7-derivative were actually synthesised or the one C-atom in question eliminated as a CO-derivative.

Dr. G. Harris Morris said that the authors' account of the action of diastase on the stable dextrin probably explained the contradictory statements which had been made by different observers as to the formation of dextrose from maltose under the action of the enzymes of germinated and ungerminated cereals. In working with pure maltose and the cold-water extracts of several cereals, he had been unable to obtain the slightest evidence of any such action except in the case of maize, but others, using malt extracts and starch-conversion products, had obtained indications of the formation of dextrose. It had been assumed that this dextrose was formed by the hydrolysis of the maltose contained in the starch-conversion products, but it would now appear that it resulted from the action of the diastase on the stable dextrin, and that his conclusion that malt obtained no] enzyme capable of hydrolysing maltose was correct.

Mr. [A. R. Ling, in commenting on the observation that the dextrinic acids were well characterised substances, thought it was unfortunate that neither they nor their derivatives were crystalline. This was, perhaps, rather remarkable in the case of the acid of lowest molecular weight. He was glad to hear that the authors had convinced themselves that the so-called stable dextrin was a cupric-reducing substance. Mr. Baker and he had submitted numerous preparations of this dextrin to dialysis and fractional precipitation with aqueous alcohol for several months, and had thus obtained a final product having approximately the same optical and reducing powers as that observed by the authors.

Mr. J. F. Briggs asked what was the relation between the stable dextrin of R 5·5 and the dextrin which Dr. Brown formerly obtained by purification by means of mercuric cyanide; the latter had practically no reducing power.

Mr. Fenton said that he was particularly interested in the C_5-acid described by the authors, as, in conjunction with Mr. Jackson, he hoped to prepare a similar acid from erythrose by the hydrogen cyanide reaction.

Dr. Brown, in reply, stated that the constitution of these reducing polysaccharides can perhaps be explained in the simplest way by regarding them as complexes built up much in the same manner as the hexose residues

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of maltose. If the currently accepted explanation of the constitution of maltose ever requires modification, this must of course modify our views as to the exact mode of combination of the constituent groups of the polysaccharides.

The constitution of the C_5-acid is at present occupying the attention of the authors. He agreed with Dr. Morris that these observations will go far to reconcile the conflicting statements with regard to the formation of dextrose from starch by diastase.

The non-reducing dextrins obtained in the older experiments by the mercuric cyanide method were no doubt maltodextrinic and dextrinic acids.

*16. "*Propylbenzenesulphonic Acids.*" By Gerald T. Moody, D.Sc.

The results described in this note have been obtained in the course of an investigation on isomeric change (*Proc.*, 1888, iv., 77; 1892, viii., 90, 213, 214; 1895, xi., 48).

Propylbenzene readily sulphonates when shaken with one and a half times its own volume of ordinary sulphuric acid, and the product consists almost entirely of one propylbenzenesulphonic acid, the amide of which melts at 109—110°. This sulphonamide, on oxidation with potassium permanganate, yields 4-sulphonamidobenzoic acid (m. p. 280°), showing that it is derived from propylbenzene-4-sulphonic acid.

Propylbenzene-3-sulphonic acid and propylbenzene-2-sulphonic acid are obtained by reducing 2-bromopropylbenzene-5(? 3)-sulphonic acid and 4-bromopropylbenzene-2-sulphonic acid respectively. Propylbenzene-3-sulphonamide melts at 57°. Propylbenzene-2 sulphonamide yields 2-sulphonamidobenzoic acid ("saccharin," m. p. 222°) on oxidation with permanganate, and melts at 128°. This melting-point is identical with that of the sulphonamide of the second acid obtained in small quantity on direct sulphonation, and is much higher than either that recorded by R. Meyer, or that by Claus for the sulphonamide obtained by them respectively from the acid which they consider to be propylbenzene-2-sulphonic acid, and regard as one of the products of direct sulphonation. It is to be noted, however, that these authors do not appear to have taken the precaution of purifying the hydrocarbon employed by them, and it is extremely likely that the fuming acid used gave rise to disulphonic acid.

Propylbenzene-3-sulphonic acid and propylbenzene-2-sulphonic acid do not undergo isomeric change when heated for several hours at 150°. The stability of the latter acid, compared with that of ethylbenzene-2-sulphonic acid, which is converted into ethylbenzene-4-sulphonic acid at the temperature of the water-bath, is remarkable, more particularly when considered in conjunction with the fact that propylbenzene-2-sulphonic acid is either not formed, or, if formed direct, is produced only in small quantity by the direct sulphonation of propylbenzene.

The author proposes next to investigate the products of sulphonation of isopropyl benzene, more particularly with reference to Claus's statement that the primary product is the parasulphonic acid, and that this is converted into ortho-derivative both on heating at the temperature of the water-bath and on allowing it to remain for ten weeks in sulphuric acid solution.

(To be continued).

PHYSICAL SOCIETY.

Annual General Meeting, February 10th, 1899.

Mr. Shelford Bidwell, F.R.S., President, in the Chair.

The Report of the Council was read by Mr. H. M. Elder.

Dr. Atkinson then presented the Treasurer's Report, and showed that, although there was only a small balance in the bank, the financial position had somewhat improved. The list of Fellows lost to the Society by death was read: the obituary includes the names of Latimer Clark, C.E., F.R.S. Sir James Douglass, F.R.S.; John Hopkinson, D.Sc., F.R.S.; J. E. Myers; Eugene Obach; Henry Perigal, F.R.A.S.; and Bartholomew Price, M.A., F.R.S.

After some remarks with regard to the library and the subscriptions, votes of thanks were passed to the Council, the Auditors, and to the other Officers of the Society.

The President then moved a vote of thanks to the Chemical Society for the use of the rooms at Burlington House.

Council and Officers for the forthcoming year were elected as follows:—

President—Oliver J. Lodge, D.Sc., F.R.S.

Vice-Presidents, who have filled the Office of President—Dr. J. H. Gladstone, F.R.S.; Prof. G. C. Foster, F.R.S.; Prof. W. G. Adams, M.A., F.R.S.; The Lord Kelvin, D.C.L., LL.D., F.R.S.; Prof. R. B. Clifton, M.A., F.R.S.; Prof. A. W. Reinold, M.A., F.R.S.; Prof. W. E. Ayrton, F.R.S.; Prof. G. F. Fitzgerald, M.A., F.R.S.; Prof. A. W. Rücker, M.A., F.R.S.; Capt. W. de W. Abney, R.E., C.B., D.C.L., F.R.S.; Shelford Bidwell, M.A., LL.B., F.R.S.

Vice-Presidents—T. H. Blakesley, M.A.; C. Vernon Boys, F.R.S.; G. Griffith, M.A.; Prof. J. Perry, D.Sc., F.R.S.

Secretaries—W. Watson, B.Sc. (Physical Laboratory, South Kensington); and H. M. Elder, M.A. (50, City Road, E.C.).

Foreign Secretary—Prof. S. P. Thompson, D.Sc., F.R.S.

Treasurer—Dr. E. Atkinson.

Librarian—W. Watson, B.Sc.

Other Members of Council—Prof. H. E. Armstrong, D.Sc., F.R.S.; Walter Baily, M.A.; R. E. Crompton; Prof. J. D. Everett, D.C.L., F.R.S.; Prof. A. Gray, LL.D., F.R.S.; E. H. Griffiths, M.A., F.R.S.; Prof. J. Viriamu Jones, M.A., F.R.S.; S. Lupton, M.A.; Prof. G. M. Minchin, M.A., F.R.S.; and J. Walker, M.A.

The newly-elected President, Prof. Oliver Lodge, then took the Chair, and an Ordinary Meeting was held. In his Address he referred to the heavy death-roll of the Society during the past year, and to the tribute paid to the memory of John Hopkinson at Cambridge University. Prof. Lodge then commented on the quickness with which scientific discoveries were now applied to practice, and to the interest taken in such applications by men of science. He did not know whether this was due to the example and inspiration of Lord Kelvin, or to the progress of education among the public. He regretted that the public was so ignorant of scientific subjects. Rapidly reviewing the work done in Physics during the past year, he spoke of the experiments of Righi, Preston, Michelson, and J. J. Thomson, and called attention to a prediction lately published in *Nature*, by Prof. G. F. Fitzgerald, with regard to the probability of being able to obtain magnetic effects by passing circularly polarised light through absorptive media. After commenting upon the important position now occupied by Terrestrial Magnetism among the Sciences, and to the advantages of the publication now known as *Science Abstracts*, Prof. Lodge said there was one event of exceptional significance to Physics that had happened during the past year, an event of which Science would feel the effect for centuries to come—the Government had decided to begin to establish a National Laboratory. He wished to congratulate Sir Douglas Galton, and himself, on the speedy result of their urging the matter upon the British Association. He thought the thanks of the Physical Society were due to the Committee appointed by the Treasury, especially perhaps to Prof. Rücker, as Acting-Chairman of that Committee, and to Mr. Chalmers, who represented the Treasury, for

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the way in which the work had been brought to an issue. There was much for which the present Government deserved praise during the past year; he wished there could be added to their laurels the inauguration of a University for London. Prof. Lodge then went on to the specific subject of his Address—the opacity of conducting media to light and to electric waves generally, emphasizing the brilliant work of Mr. Oliver Heaviside in unifying phenomena apparently different, discussing the effect of boundaries, and dealing specially with the question—first attacked by Maxwell—of the theoretical opacity of gold-leaf. This part of the Address will be published in full in the *Phil. Magazine*.

Prof. Ayrton said, with regard to the attenuation of electric waves by the earth, that Mr. Whitehead, some months ago, came to the conclusion that when the primary and secondary coils were placed flat on the earth, at a distance from one another, nearly all the energy of the primary was absorbed by the earth before reaching the secondary. The degree of absorption was so great that Mr. Whitehead had hesitated to publish his theoretical results until experiment should confirm them.

Prof. Lodge concurred with Mr. Whitehead's result. Three cases were to be considered. In the first, one horizontal coil is superposed to the other, with sea-water or some other absorbing medium between them; in this case the absorption at moderate distances is not excessive. But of course if the coils are formed of cable sheathed with iron, as in the recent experiments made by the Royal Commission, the iron itself prevents the progress of electric waves from primary to secondary. In the second case the coils are wholly in the same horizontal plane: the earth, owing to its great magnitude, behaves almost as a perfect conductor; if the coils are now near the earth, there is no normal magnetic force between them—it is all tangential. In the third case the coils are opposed to one another, both being vertical and near to the earth. The high conductivity of the earth is here acting to the advantage of wave propagation, for the image of the primary coil is in phase with the coil itself, and the total effect is approximately doubled.

Prof. Carey Foster then took the Chair, and Prof. Oliver Lodge read a paper by Mr. Benjamin Davies on "*A New Form of Ampere-meter and Voltmeter with a Long Scale.*" These instruments are already well known, although no account of them has actually been published. They are of the moving-coil, long-range, portable type, with a very uniform scale from zero to maximum. The magnetic circuit has only one air-gap, which is generally the space between a central cylinder of iron or steel and a concentric tube of iron, modified in various ways for facilitating the adjustment of the magnetic induction and the placing of the coil. The central cylinder is bored axially, and one side of the rectangular coil is pivoted at the top and bottom of the hole thus made. The second side of the coil moves in a circular path in the annular air-gap. Photographs of the instruments in several modified forms were exhibited.

Prof. Ayrton said the instruments appeared to be very successful; he could bear witness of their value particularly as regards the length of range. The general principle by which long range was to be obtained on moving-coil, portable instruments, was developed some ten years ago by M. Carpentier, of Paris, who used a central magnet surrounded by a concentric hollow cylinder, with only one side of the coil in the magnetic gap between them; but it was not then a portable form of instrument, for the coil was suspended. Prof. Ayrton had himself worked in this direction in the "static station volt-meter." In that instrument there were three magnetic circuits arranged to give staticism; this was described in 1892 or 1893.

The Vice-President (Prof. Carey Foster) proposed a vote of thanks to the author, and the meeting adjourned until February 24th.

NOTICES OF BOOKS.

Electrolysis and Electrosynthesis of Organic Compounds. By Walther Loeb. Authorised Translation from the Author's Enlarged and Revised Edition, by H. W. F. Lorenz. New York: John Wiley and Sons. London: Chapman and Hall, Limited. 1898. Pp. xiii.—103. 12mo.

The electrolysis of inorganic compounds has obtained a recognised position in pure and applied science, but the great difficulties attending attempts to carry out the synthesis or decomposition of organic compounds has prevented securing entirely satisfactory results. In inorganic electrolysis the development has been regular and systematic, but organic compounds yield such diverse and complex results that the history of this branch of electrolysis is largely a collection of incoherent facts. Feeling this, Dr. Loeb undertook to compile, from the literature scattered through numberless periodicals, a summary of the investigations of the many workers in this fertile field. Such was the origin of the little book which now appears in an English dress. The investigations summarised are arranged in systematic order—hydroxyl compounds, ketones, acids, &c. Due credit is given to the several chemists for their part in each case, and in nearly all cases references to literature are given, so that the footnotes constitute a bibliography of the subject.

Some of the processes have become of industrial value, the preparation of iodoform by the electrolysis of ethyl alcohol in alkaline iodide solution is an example; and patents have been taken out for the preparation of valuable substances in the aromatic series.

The book is a very useful summary; the translator has done his work well. The abbreviation "Chem. Ber." for "Ber. d. Chem. Ges." looks unfamiliar. A key to abbreviations might be added in a second edition. The chief blemish to this work is the absence of dates in connection with references to periodical literature.

H. C. B.

An Experimental Course of Chemistry for Agricultural Students. By T. S. Dymond, F.I.C., Lecturer on Chemistry and Agricultural Chemistry in the County Technical Laboratories, Chelmsford. London: Edward Arnold, 37, Bedford Street, Strand.

This work, under the general editorship of Professor R. Meldola, F.R.S., is intended to meet the needs of agricultural students in the rural districts, the special aim being to give the intending farmer training in accuracy, careful observation, and a knowledge of the elementary principles of chemical change and of the properties of certain chemical substances, both organic and inorganic.

As the customary four years' course of organic and inorganic chemistry goes far beyond the requirements of an agricultural student, the present course has been restricted as far as possible to the study of the chemical substances with which agriculture is concerned.

There are plenty of illustrations, and the problems set for the student are clear and to the point, and, if conscientiously worked out, cannot fail to be of great value.

Practical Inorganic Chemistry for Advanced Students. By Chapman Jones, F.I.C. London: Macmillan and Co. 1898. Pp. 239.

We object to part of the title the author has chosen for his book: instead of "advanced students" he should have said "beginners." He tells us that this text-book is specially intended for the use of students working according to the arrangements made by the Department of Science and Art, but the bulk of the information herein

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given should be acquired by first year's students, or "beginners." We cannot imagine an advanced student requiring a description accompanied by an illustration, as on page 48, of how to make a loop at the end of a platinum wire.

The book is divided into three parts. Part I. on preparations, and exercises in manipulation, including the preparation of gases by the use of hot and cold liquids and dry substances, distillation, &c. Part II. introduces qualitative analysis, and deals *seriatim* with the five groups and their sections; and in Part III. we have quantitative volumetric analysis, and the preparation of standard solutions.

The Smithsonian Institution, 1846—1896. The History of its First Half-century. Edited by GEORGE BROWN GOODE. City of Washington. 1897. Pp. 856.

THE Smithsonian Institute was established in 1846, by a law signed by President Polk on the 10th August of that year, and the first meeting of the Board of Regents was held on the 7th September following. The splendid volume now before us gives the history of this Institution from that time to the end of its first fifty years of existence.

The plan of the volume was drawn up by Dr. G. Brown Goode, and, on its approval, the editing was undertaken by the late Dr. James C. Welling. The unfortunate death of this gentleman, however, greatly delayed the work, until it was undertaken and carried to a successful issue by Dr. Goode.

The book begins with a short Preface by the President of the United States, the remainder being divided into two great Sections. Section I., of fifteen chapters, is entitled "History of the Smithsonian Institution," and Section II., also of fifteen chapters, is called "Appreciations of the Work of the Smithsonian Institution."

In Section I. we first find a biography of James Smithson, who was, through his mother, lineally descended from Henry VII. of England: this is followed by chapters on the founding of the Institution, the establishment of the Board of Regents, the Secretaries, the Benefactors, the Buildings, Grounds, Library, Museums, &c. The publications and exploration works of the Institute are also dealt with by competent writers, and the Section closes with a biographical sketch of Dr. G. Brown Goode, by David S. Jordan.

Section II. consists of a series of essays and monographs on the various scientific subjects which have engaged the attention of the Smithsonian Institution; thus we have Physics by Prof. Mendenhall, Astronomy by Edward S. Holden of the Lick Observatory, Palæontology by Prof. Cope, Zoology by Prof. Gill, and Bibliography by Prof. H. Carrington Bolton, &c.

The book is adorned with a number of excellent portraits; it is well printed in clear bold type, and will be an ornament to any library.

Calculations concerning Water-pipes. ("Kálkulos sobre las Kañerias de Agua"). By A. E. SALAZAR, Professor of Physics at the University of Chile. With the Original Diagrams and Tables. Santiago de Chile: Hume I Ka, Armada. 1898. Pp. 246.

THIS is essentially a mathematical work for water engineers, and deals entirely with calculations for determining the size, shape, and positions of water-pipes and aqueducts, with regard to the flow of water through them, with respect to both rate and power, loss by friction, &c., and with hydraulics and turbines.

The book is divided into eight chapters and an Appendix, there are seventeen figures and ten tables, as well as a good Index. The book is printed on good paper, and, unlike most foreign works, is well bound in a stiff cover.

CORRESPONDENCE.

THE ESTIMATION OF MANGANESE BY MEANS OF POTASSIUM PERMANGANATE.

To the Editor of the Chemical News.

SIR,—I have to thank Mr. F. W. Daw for his opinion as to the cause of the low results when a permanganate solution standardised with iron is used to titrate manganous salts.

He says "that the usually accepted equation for the action of permanganate on manganous sulphate does not, *in the circumstances under discussion*, quite represent the reaction taking place." This statement does not convey the information it was intended to, because I do not know whether the phrase italicised refers to the circumstances under which I worked when the low results were attributed to traces of carbon in the iron, or to the circumstances he describes in his recent article (CHEM. NEWS, lxxix., 25). The importance of this distinction lies in the fear that the separate processes would give different results when the same sample was operated upon. The fact is that the precipitated oxides of manganese approximate variously to MnO_2 with varying modes of procedure, and from the work of Wright and Menke (*Journ. Chem. Soc.*, 1880, p. 36) it might be inferred that the oxides precipitated by Mr. Daw's procedure are deficient in oxygen.

I was not unaware of the work of Gooch and Austen, to which my attention is next called. It is only fair, however, to say that under what they consider the best circumstances their opinion of the method is little short of the "faint praise which damns." For instance, it is certainly unfortunate that the experimentalists on whom whom Mr. Daw leans should say "The inference is plain that the estimation of manganese in the form of mangonoso-manganic oxide, Mn_3O_4, is by no means to be considered utterly untrustworthy when the process is conducted in the manner described, though it must be recognised that an irregular result may occur occasionally." This is hardly a satisfactory recommendation for a standardisation process at all, much less for a process by the results of which the validity of this or that means of standardising shall be measured.

So as not to be misunderstood, I must remark that it is not the weighing as Mn_3O_4 which I have questioned, but only the final heating of it, in platinum crucibles, over a naked Bunsen flame. That this practice is fraught with danger is shown by the experience of Wright and Luff (*Journ. Chem. Soc.*, 1878, p. 520), who obtained a manganoso-manganic compound, containing too much oxygen, and by Pickering (CHEM. NEWS, xliii., 226) who found the percentage of manganese vary from 69·688 to 74·997. These results have been used to good purpose by those chemists who favoured the precipitation of manganese as the ammonium phosphate and the weighing as pyrophosphate.

Morse and Burton (*Am. Chem. Journ.*, x., 2, and CHEM. NEWS, lvii., 176) showed that the constant loss of weight when zinc oxide is heated in platinum vessels over a gas flame is due to the permeability of that metal to reducing gases, an explanation which Pickering had previously suggested to account for his variant manganese results. Since that time I believe that generally direct contact of flame has been avoided. This much is certain, that Wright and Luff found strong ignition, *after surrounding the capsule with a clay jacketing*, to yield a compound closely approximating to Mn_3O_4; that Fresenius ("Quant. Anal.," p. 202, 7th ed.), says the oxides, *ignited out of contact with reducing gases*, gives Mn_3O_4; and that nearly every writer who recommends this method of estimating manganese especially mentions strong ignition *in a muffle furnace*.

I beg, finally, to say that I have never been seriously engaged, experimentally, with the points under discussion;

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I therefore write by no means dogmatically. At the same time I have been so far interested as to read whatever papers of a relevant nature were available, and the almost unanimous opinion seems to be that, although it is not *impossible* to produce Mn_3O_4 in the way Mr. Daw describes, it certainly is not a good method to employ.—I am, &c.,

HARRY BREARLEY.

Totley, near Sheffield.

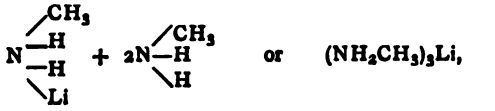
CHEMICAL NOTICES FROM FOREIGN SOURCES.

NOTE.—All degrees of temperature are Centigrade unless otherwise expressed.

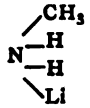
Comptes Rendus Hebdomadaires des Séances, de l'Académie des Sciences. Vol. cxxviii., No. 1, January 2, 1899.

General Method of Separating Mixtures of Chloride, Bromide, and Iodide of Silver.—H. Baubigny.—The author refers to the beginning of this research which he has already published, and he now states that he has confirmed his former method of separating chloride, bromide, and iodide of silver quantitatively. The method of employing oxidising agents is a practical and rapid method of recognising the presence of bromine in a mixture of silver halogen salts. The precipitate, whilst still wet, is treated with nitric acid and crystals of permanganate. This mixture transforms the iodide into iodate, and does not sensibly act on silver chloride, whilst the bromide is attacked very slowly. As fluorescin paper is exceedingly sensitive to bromine vapour, mere traces can be detected with certainty.

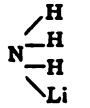
Preparation and Properties of Lithium-Monomethylammonium.—Henri Moissan.—This paper deals with the extension to compound ammonias of the reaction by which lithium-ammonium and calcium-ammonium were obtained. The cases of liquefied methylamine in contact with the metals potassium, sodium, lithium, and calcium were investigated. At temperatures between $+20°$ and $-50°$ potassium, sodium, and calcium gave no immediate or subsequent combination. Lithium, on the contrary, gave a blue solution, with evolution of heat; towards $0°$ the composition of this product approximates to the formula—



and should be regarded as a solution of the lithium-methylammonium in methylamine. On allowing the compound to dissociate, either in vacuo at the ordinary temperature, or by warming, till a small quantity of the metal appears permanently, a blue solid body is easily obtained, corresponding to the formula—



which is an organic ammonium analogous to lithium-ammonium—



It is stable at ordinary temperatures; reacts with violence on carbon tetrachloride, chloroform, and ethyl iodide; fixes oxygen and nitrogen in the cold, but has no action on hydrogen.

MEETINGS FOR THE WEEK.

MONDAY, 20th.—Society of Arts, 8 (Cantor Lectures). "Cycle Construction and Design," by Archibald Sharpe, A.M.Inst.C.E.

TUESDAY, 21st.—Royal Institution, 3. "The Morphology of the Mollusca," by Prof. E. Ray Lankester, M.A., LL.D.

—— Society of Arts, 8. "Vitreous Enamels," by Cyril Davenport.

WEDNESDAY, 22nd.—Society of Arts, 8. "Electric Traction and its Application to Railway Work," by Philip Dawson.

THURSDAY, 23rd.—Royal Institution, 3. "Toxins and Antitoxins," by Dr. Allan Macfadyen, M.R.C.S.

FRIDAY, 24th.—Royal Institution, 9. "Coherers," by Prof. Oliver Lodge, F.R.S., &c.

—— Physical, 5. "The Joule-Thomson Thermal Effect," by E. F. J. Love, M.A. "A Study of an Apparatus for the Determination of the Rate of Diffusion of Solids dissolved in Liquids" and "Note on the Source of Energy in Diffusive Convection," by Albert Griffiths, M.Sc.

SATURDAY, 25th.—Royal Institution, 3. "The Mechanical Properties of Bodies," by The Right Hon. Lord Rayleigh, F.R.S., &c.

TO CORRESPONDENTS.

C. B. H. D.—A complete list of elements, with their atomic weights, will be found in our last volume (CHEM. NEWS, vol. lxxviii., p. 194).

The BIRMINGHAM TAME AND REA DISTRICT DRAINAGE BOARD require the services of a properly qualified ANALYTICAL CHEMIST to act under the general direction of the Engineer in connection with the Board's Sewage Purification Works.

He must have had practical experience in the Quantitative and Qualitative Analysis of Water and Sewage. Experience in Bacteriological Investigations will be considered an additional qualification.

Commencing Salary, £135 per annum, rising to £165 per annum.

The appointment to be subject to One Month's Notice on either side.

Applications, stating age and qualifications, and endorsed "Analyst," together with not more than three recent testimonials, to be sent to me not later than March 6th, 1899.

(By Order) J. KNIGHT,
Offices of the Drainage Board, Engineer to the Board.
Council House, Birmingham,
February 14th, 1899.

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THE CHEMICAL NEWS.

Vol. LXXIX., No. 2048.

MODIFIED FORMS OF APPARATUS FOR THE ESTIMATION OF HALOGENS AND OF AMMONIA.

By F. D. CHATTAWAY, M.A., and K. J. P. ORTON, M.A.

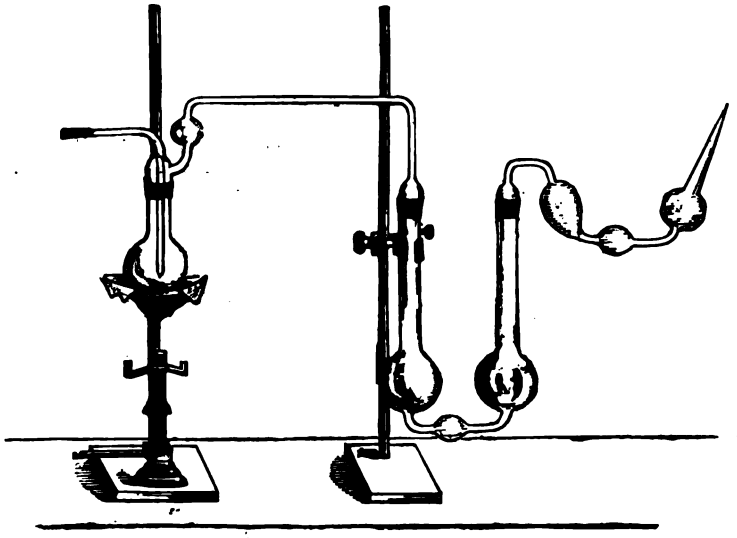
The apparatus ordinarily figured in text-books for use in the volumetric estimation of a halogen or of ammonia is not very convenient. We have recently had occasion to make a large number of such analyses, and have employed modifications which may prove of service to other chemists.

Apparatus for Estimation of Halogens by Distilling them into a Solution of Potassium Iodide.

This (Fig. 1) consists of a flask of about 300 c.c. capacity, closed by a hollow ground-glass stopper into which are sealed two tubes, one of narrow bore leading to the bottom of the flask, and the other of wider bore, blown into a bulb above the stopper, connecting the flask with a U-tube which is attached by its other limb to an absorption apparatus.

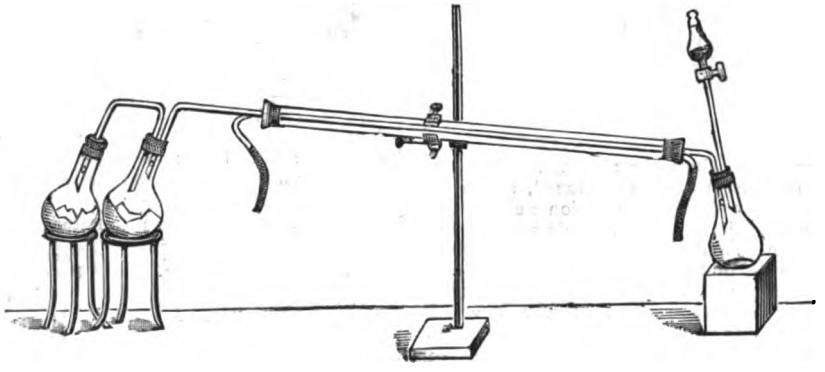
The parts are all carefully ground together, so that the evolved halogen can never come into contact with any oxidisable material—an absolutely essential point if great accuracy be needed. The distillation is conducted in a slow stream of carbon dioxide, led to the bottom of the flask by the fine tube. This ensures regular boiling, so that the distillation requires little attention, and prevents any oxidation of the hydriodic acid, which, when acid solutions are distilled, is always liberated from the potassium iodide used to retain the product. As a further protection it is advisable to add a little finely-powdered calcium carbonate to the potassium iodide solution.

The U-tube is cooled in a beaker of water, and it is well to wrap a piece of filter-paper round the limb heated by the steam, keeping it moist by allowing it to dip below the surface. The apparatus is somewhat cheaper and very little less efficient if the final absorption bulbs, which are used to prevent any possible loss of iodine, are connected with the U-tube by an indiarubber stopper, but the distillation cannot then be carried out so quickly.



$\frac{1}{10}^{TH}$ ACTUAL SIZE

Fig. 1.



$\frac{1}{12}^{TH}$ ACTUAL SIZE

Fig. 2.

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Apparatus for Estimation of Ammonia or of Nitrates and Nitrites by Reduction.

This (Fig. 2) is a modification of Harcourt's apparatus (*Journ. Chem. Soc.*, xv., 385).

The ends of the bent inner tube of the condenser and of the tube connecting the distilling flasks are cut or ground off at a sharp angle, and in each, except the delivery tube into the second flask, a small hole is blown about 2 c.m. below the stopper.

The inner condenser-tube is bent at its lower end, so as to pass vertically into a 300 c.c. flask which serves as a receiver. Through the stopper of this flask also passes the stem of a tap funnel which is half filled with glass beads. Standard acid is added to the receiver through the tap funnel, which serves as a very efficient scrubber.

The second flask should be boiling quietly before the first flask containing the alkaline liquid is heated; twenty to thirty minutes' boiling is sufficient to complete an ammonia distillation. On detaching the flask and rinsing out into it the tap funnel and the end of the condenser tube through the small hole, the contents are ready for titration.

The distilling flasks in this and the preceding apparatus are conveniently heated in cups made of thin asbestos board, or thicker board split; this is soaked with water, moulded to the shape of the flask, then dried and detached. Such cups prevent bumping in most cases.

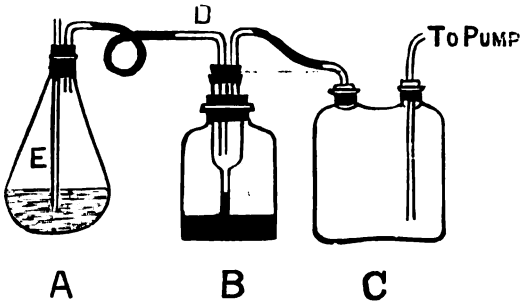
Chemical Laboratory,
St. Bartholomew's Hospital, E.C.

A FILTER PUMP ACCESSORY.

By HORACE JERVIS.

Three years ago (Chem. News, lxxiv., 63) there was described an arrangement for agitating liquids by drawing a current of air through a series of properly fitted and arranged flasks by means of an ordinary filter-tube or pump. The apparatus is described in connection with its use in dissolving steel in copper ammonium chloride solution; it is in this same capacity I have had experience with it.

Until a few months ago a particular filter-tube was supplied with water from a cistern. For certain reasons the supply had to be drawn directly from the main, which, as we were placed higher than any other users on the same service, caused the supply to be very irregular in amount when the cock remained a fixed distance open.



On several occasions since the alteration was made it has happened that the suction has ceased, and a back pressure has pushed the copper solution nearly, if not altogether, into the adjacent flasks. This appears to be caused by a sudden rush of water having no easier means of escape than *up* the tube into the reservoir bottle C (see figure). I have known a similar effect to be due to the stopping up of one of the inlet tubes, whereby the vacuum became great enough to draw the water the wrong way.

From the former cause the occurrence has become frequent enough to warrant special precautions being taken to prevent it. Where the agitated liquid would leave no trace, did such a thing happen, some precaution seems advisable, even if the danger appears remote.

The figure represents the reservoir bottle, C, the dissolving flask, A, and the safety arrangement, B, when the operation is proceeding as usual. The latter piece of apparatus is one of several forms which have been tried. It is particularly chosen for illustration because it can be made to serve a double purpose.

A verbal description is hardly necessary. The drawn out tube is held firmly, but not air-tight, in the neck of the bottle; its tip dips just below the surface of the mercury. No air can be drawn through this arrangement, because the tube is so narrowed that a considerable pressure can be indicated without sensibly lowering the general level of mercury; but if from any cause the water runs back into C, the compressed air finds escape by pushing the mercury below the bottom of the drawn out tube before the solution in the dissolving flask is pushed beyond any desired point on the straight tube, E. (This statement becomes less and less true as the number of flasks are increased). There is thus no possibility of copper solution passing from one flask to the other.

By pouring mercury into the bottle until it nearly reaches the lower end of the larger tube D, which passes through the doubly perforated stopper, the apparatus becomes also an arrangement whereby the degree of exhaustion is kept constant. As soon as the pump is started, mercury rises so far that the end of the tube D is covered; after that varying suction is exactly counterbalanced by the varying height to which the mercury will rise.

The first of these purposes is most simply accomplished by allowing a drawn out leg of a three-way tube, whose other ends are attached to A and C, to pass into a bottle containing mercury. The latter purpose, I am reminded, is more elaborately, and perhaps better, accomplished by a piece of apparatus used by Theo. W. Richards in connection with vapour density determinations under reduced pressure (Chem. News, lix., 39).

THE PRODUCTION OF CHLORATES BY ELECTROLYSIS FROM SOLUTIONS OF CHLORIDE OF CALCIUM.

By F. CETTEL.

The results I have obtained by the electrolysis of solutions of chloride of calcium confirm the indications recently furnished by Bischoff and Fœrster. The very slight importance of the losses by reduction is attributed to the formation of a thin layer of hydrate of calcium on the cathode; this layer acts as a diaphragm. The electro-chemical activity of this slight skin does not, however, appear to depend upon its being thick; since, on the one hand, excellent results have been obtained with an extremely thin membrane; and, on the other hand, a diaphragm of 2 m.m. in thickness was practically without effect. The production—and what is of more importance, the preservation—of a good membrane requires great care and experience.

The following table shows the normal course of an electrolysis. The solution of chloride of calcium contained 130—150 grms. of the salt per litre, and a little milk of lime was added to precipitate the magnesia. The density of the current was 900 ampères per square metre of anode and cathode; the difference of potential varied between 3·8 and 4 volts, and the temperature was kept up to 75° C.

Duration from the commencement. Hours.	Useful return from the current. Per cent.	Decomposition of water. Per cent.	Reduction. Per cent.
¼	71·8	4·1	24·1
½	76·3	11·4	12·3
1	78·2	12·5	9·3
3	79·7	16·5	3·8
5	83·1	12·9	4·0
8	81·1	12·5	6·4
10	81·9	11·4	6·7
22	83·3	12·5	4·2

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It should be noted that the useful return from the current increases during the first few hours, and then remains practically constant at about 80 per cent.

The distribution of the remaining 20 per cent between the decomposition of water and the reduction of the already-formed hypochlorite is very variable.

In another experiment I obtained:—

Useful return from the current ..	79	per cent
Decomposition of water..	9	,,
Reduction	12	,,
	100	,,

These results were considered to be very satisfactory, and I have endeavoured to utilise them for the following purposes:—

1. To electrolyse chloride of calcium to form chlorate.
2. By adding chloride of potassium to precipitate chlorate of potassium, and thus re-generate the chloride of lime to be electrolysed over again.

By following this plan I obtained some altogether unexpected results. The presence of chloride of potassium in the solution caused the formation of thick crusts on the cathode. These crusts were gradually destroyed, and at the same time free chlorine (not hypochlorous acid) was given off simultaneously with hydrogen. I was led to the conclusion that the character of the deposit formed on the cathode is such that it cannot re-dissolve with sufficient rapidity to fix the chlorine. Further, the properties of this deposit are very variable. In one experiment a thin layer was sufficient to stop the disengagement of chlorine; in another trial, the layer disappeared completely, to give place to the thick crusts I have just spoken about, while at the same time chlorine was evolved.

By cooling the electrolyte, I could often obtain crystals of oxychloride of calcium in long needles; and I have every reason to believe that this substance plays an important part in the electrolysis.

It is possible that the curious phenomenon I observed on the addition of chloride of potassium to the solution may be connected with, not the formation, but the solubility of the oxychloride in the chloride of potassium, and that the crusts which are formed on the cathode are not the hydrate, but an insoluble oxychloride of calcium.

The electrolysis of solutions of chloride of calcium is further subject to other disturbing influences. In one experiment I performed, a quantity of chloride of copper which had formed on the surface of one of the conductors became detached from the wire and fell into the electrolytic bath, where it was transformed into oxide. This oxide, acting in its turn on the hypochlorite, decomposed it, at the same time setting free a quantity of oxygen. Other analogous substances, such as the oxides of iron, nickel, and lead, act in a similar manner, so that all sorts of precautions must be constantly taken if we wish to judge the results of an experiment from a single analysis of the gas.

This point appears to be well established by the following figures, obtained by the electrolysis of chloride of calcium in the presence of oxide of copper.

	Useful return from the current. Per cent.	Decomposition of water. Per cent.	Reduction. Per cent.
Apparent	30·9	57·2	11·9
Real	73·3	14·7	12·0

The second—or true—figures were obtained by calculations based on the measurement of the oxygen given off by the action of the oxide of copper during the same time (three minutes)—the circuit being open. From the results I have obtained I am brought to the conclusion that the electrolytic production of chlorates is accomplished by two distinct actions, which may, however, be sometimes combined:—

a. The production of the chlorate by the intermediary of the hypochlorite. The first products formed (alkali and chlorine) combine to form the hypochlorite. This hypochlorite, under the further action of the chlorine, and also by simultaneous direct oxidation, is transformed into chlorate.

b. The production of chlorate by the direct union of the chlorine and oxygen simultaneously set free at the anode.

In a neutral solution it is the *a* reaction that predominates. In a strongly alkaline solution, the other (*b*) reaction occurs. Finally, in a slightly alkaline solution, the two reactions take place simultaneously; it being always understood that the density of the current is the same in each case.

In the electrolysis of chloride of calcium in particular, the *a* reaction is the predominating one. Similar solutions show a tendency to become slightly acid on account of the formation of free hypochlorous acid. In the case of alkaline chlorides, the position of the electrodes and the density of the current are the principal causes which influence both the liberation of chlorine and the formation of a slight excess of free alkali.—*Zeitschrift für Electrochemie*, v., [1], 1—5.

THE ESTIMATION OF PHOSPHORIC ACID IN SUPERPHOSPHATES.

By LEO VIGNON.

As is well known, the estimation of soluble phosphoric acid in superphosphates and in chemical manures comprises practically three cases:—

1. Estimation of the phosphoric acid soluble in water.
2. Estimation of the phosphoric acid soluble in water and the phosphoric acid soluble in citrate of ammonia *together*.
3. Separate estimations of the phosphoric acid soluble in water and that soluble in citrate of ammonia.

The experiments described in this paper have to do only with the last case.

For the separate estimation of the phosphoric acid soluble in water and that soluble in citrate of ammonia it is usual to proceed in the following manner:—

The phosphate is first exhausted with water, then the residue is collected and treated with citrate of ammonia. We then precipitate *separately* the phosphoric acid in both the aqueous and citrate solutions in the state of ammoniomagnesic phosphate. All these operations must be carried out strictly according to the rules laid down by the Committee of Agronomic Stations and Agricultural Laboratories.

I have observed that if the sample contains much phosphoric acid soluble in water and only a small quantity soluble in citrate of ammonia, the precipitation of the latter form of phosphoric acid is not always complete, even after standing for several hours.

Samples of superphosphates treated in the way I have just described have given the following results:—

1. *After Eight Hours.*

	Bone superphosphates.	Mineral superphosphates.	
	I.	II.	III.
Phosphoric acid soluble in water	14·32	14·13	10·20
,, ,, ,, citrate	0·77	0·27	3·10
Total	15·09	14·40	13·30

2. *After Fifteen Hours.*

Phosphoric acid soluble in water	14·32	14·13	10·20
,, ,, ,, citrate	1·08	0·45	3·18
Total	15·49	14·58	13·38

The results are again different if we first mix the aqueous solution with the solution obtained by exhausting

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with citrate of ammonia. In fact, for the superphosphate examined I obtained after standing for twelve hours :—

	Bone superphosphates.	Mineral superphosphates.	
	I.	II.	III.
Phosphoric acid soluble in water and in citrate (mixed)	17·79	13·94	14·91

From which we deduce—

Phosphoric Acid Soluble in Citrate.

By direct estimation	1·08	0·45	3·18
By difference	3·47	0·81	3·71

We are thus liable, by direct estimation, to find too low figures for the phosphoric acid soluble in the citrate when it is only present in small quantities. It is true that the formation of the ammonio-magnesic phosphate may be helped by continuous mechanical agitation, and by raising the temperature to 25—30°; but these conditions complicate the analysis, and besides may not always be convenient to apply. The method of estimation by difference is more to be trusted.

It is easy to understand why the ammonio-magnesic phosphate, by reason of its mass, has a greater tendency to come down integrally in a shorter time in the aqueous and citrate mixture than in the citrate alone, which might be very poor in phosphoric acid.

To sum up, for *separate* estimations, in a superphosphate or in a manure, of phosphoric acid soluble in water and the same soluble in citrate of ammonia, it is better to estimate the phosphoric acid soluble in water *directly*, the phosphoric acid soluble both in water and citrate of ammonia *together*, and the phosphoric acid soluble in citrate of ammonia only *by difference.—Bull. Soc. Chim.*, Series 3, vol. xix.-xx., No. 20-21.

THE PURIFICATION OF ACETYLENE.

By P. WOLFF.

Hardly a day passes without some new method for the purification of acetylene being proposed with the object of preventing the formation of smoke, which always accompanies the combustion of this gas. This smoke is due to the polymerisation of the acetylene itself; it can therefore only be prevented by using special burners, and not by further purifying an already sufficiently pure gas.

Ferric hydrate, Laming's mixture, or any other analogous product, can be used for absorbing the ammonia and the sulphuretted hydrogen; but they do not absorb the phosphoretted hydrogen, which really constitutes the only objectionable impurity. To absorb this gas, Lunge and Cedercreutz have proposed the use of chloride of lime, which plays the part of an oxidising agent (*Journ. Soc. Chem. Ind.*, 1897, p. 1046).

Now, previous experiments showed the author that the action of chloride of lime on acetylene is accompanied by small explosions, following the formation of chloride of nitrogen at the expense of the chlorine of the chloride of lime and of the nitrogen of the ammonia which is always to be found in acetylene. It is therefore necessary to free the acetylene of its ammonia before purifying it with chloride of lime. This can be thoroughly done by simply washing with water. Chloride of lime can absorb phosphide of hydrogen at the same time as the sulphydric gas without danger. Thus purified, acetylene possesses only a faint ethereal odour, which should, if possible, be accentuated, for facilitating the detection of leaks. This can be effected by mixing with it a small quantity of carbylamine or acetate of amyl, or, again, by simply passing it over carbide of calcium. The act of drying by contact with this body causes the liberation of a small quantity of raw acetylene, which communicates sufficient smell without contaminating it to any appreciable extent.

Pure acetylene does not attack copper or its alloys, but any trace of impurities quickly causes brown stains to appear on polished bronze ornaments. These stains are formed of phosphide, and not acetylide, of copper.—*Chemiker Zeitung*, xxii., [28], p. 281.

LONDON WATER SUPPLY.

REPORT ON THE COMPOSITION AND QUALITY OF DAILY SAMPLES OF THE WATER SUPPLIED TO LONDON FOR THE MONTH ENDING JANUARY 31ST, 1899.

By SIR WILLIAM CROOKES, F.R.S.,
and
PROFESSOR DEWAR, F.R.S.

To MAJOR-GENERAL A. DE COURCY SCOTT, R.E.,
Water Examiner, Metropolis Water Act, 1871.

London, February 10th, 1899.

Sir,—We submit herewith, at the request of the Directors, the results of our analyses of the 182 samples of water collected by us during the past month, at the several places and on the several days indicated, from the mains of the London Water Companies taking their supply from the Thames and Lea.

In Table I. we have recorded the analyses in detail of samples, one taken daily, from Jan. 1st to Jan. 31st inclusive. The purity of the water, in respect to organic matter, has been determined by the Oxygen and Combustion processes; and the results of our analyses by these methods are stated in Columns XIV. to XVIII.

We have recorded in Table II. the tint of the several samples of water, as determined by the colour-meter described in previous reports.

In Table III. we have recorded the oxygen required to oxidise the organic matter in all the samples submitted to analysis.

Of the 182 samples examined by us during the month, all were found to be clear, bright, and well filtered.

There has been a considerable excess of rain during during January, the actual fall at Oxford was 2·85 inches, the average fall for the past thirty years is 2·16 inches; this gives an excess of 0·69 inch, or 31·9 per cent.

Our bacteriological examinations of 255 samples have given the results recorded in the following table; we have also examined 37 other samples, from special wells, standpipes, &c., making a total of 292 samples in all :—

	Microbes per c.c.
New River, unfiltered (mean of 25 samples) ..	1651
New River, filtered (mean of 25 samples) ..	11
Thames, unfiltered (mean of 25 samples) ..	22764
Thames water, from the clear water wells of five Thames-derived supplies (mean of 128 samples)	35
Ditto ditto .. .. highest	260
Ditto ditto .. .. lowest	0
River Lea, unfiltered (mean of 26 samples) ..	4576
River Lea, from the East London Company's clear water well (mean of 26 samples) . ..	14

The above figures show the average bacteriological condition of the London waters to be highly satisfactory, being only 35 microbes per cubic centimetre although the crude Thames water contained upwards of 22,000 per c.c.; this shows a very high efficiency of filtration. It will be observed that one sample gave an abnormal result, namely, 260 microbes per c.c. This was caused by a temporary defect in a filter, which was immediately detected by us, and at once attended to.

We are, Sir,
Your obedient Servants,
WILLIAM CROOKES.
JAMES DEWAR.

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DERIVATIVES OF THE TETRABROMIDES OF ZIRCONIUM AND THORIUM.*

By J. MERRITT MATTHEWS.

1.—Introduction.

This investigation was taken up as an adjunct to a preceding research (*Journ. Am. Chem. Soc.*, xx., p. 815; Chem. News, lxxix., p. 6) on the Derivatives of the Tetrachlorides.

Only derivatives with the four most typical amines—ammonia, ethylamine, aniline, and pyridine—were prepared, as it was considered needless to extend the investigation further, when the aim was only to prove a general reaction between the amine bases and the tetrahalides of the fourth group.

The anhydrous tetrabromides of zirconium and thorium were prepared in a manner exactly similar to their tetrachlorides, dry bromine vapours in a current of carbon dioxide gas being substituted for chlorine (Mellis, *Ztschr. Chem.*, [2], vi., 296; Troost and Ouvrard, *Ann. Chim. Phys.*, [6], xvii., 229).

Owing to the slight solubility of the tetrabromides in any of the usual organic solvents, the reagents in all cases were added to the dry salts, any excess being removed by washing the product so formed with ether.

Several attempts were made to prepare the tetrabromide of lead, proceeding in a manner analogous to that used in the preparation of the tetrachloride, but without success.

2.—The Amine Derivatives.

A. *Ammonia.*

a. Zirconium Tetrabromide, $ZrBr_4.4NH_3$.—On passing dry ammonia gas over zirconium tetrabromide at a slightly elevated temperature, a white compound was formed.

0·5186 grm. zirconium tetrabromide increased in weight to 0·6035 grm.

0·2246 grm. of this compound on analysis gave:—

0·3511 grm. silver bromide = 0·1494 grm. bromine = 66·50 per cent bromine.

0·0584 grm. zirconium dioxide = 0·0432 grm. zirconium = 19·22 per cent zirconium.

0·3024 grm. material gave:—

0·2426 grm. platinum = 0·0422 grm. ammonia = 13·96 per cent ammonia.

	Calculated for $ZrBr_4.4NH_3$.	Found.
Bromine	66·80	66·50
Zirconium	18·96	19·22
Ammonia	14·23	13·96
	Grm.	Grm.
Increase in weight	0·0861	0·0849

b. Thorium Tetrabromide, $ThBr_4.3NH_3$.—This was prepared in the same manner as the zirconium compound, and was white in colour.

0·4712 grm. thorium tetrabromide increased in weight to 0·5119 grm., which on analysis gave:—

0·6491 grm. silver bromide = 0·2762 grm. bromine = 53·96 per cent bromine.

0·2273 grm. thorium dioxide = 0·1997 grm. thorium = 39·01 per cent thorium.

	Calculated for $ThBr_4.3NH_3$.	Found.
Bromine	53·07	53·96
Thorium	38·47	39·01
	Grm.	Grm.
Increase in weight	0·0435	0·0407

B. *Ethylamine.*

a. Zirconium Tetrabromide, $ZrBr_4.4C_2H_5NH_2$.—0·2506 grm. zirconium tetrabromide, treated with ethylamine, gave 0·3572 grm. of a white compound, which on analysis yielded:—

0·4597 grm. silver bromide = 0·1956 grm. bromine = 54·75 per cent bromine.

0·0769 grm. zirconium dioxide = 0·0569 grm. zirconium = 15·92 per cent zirconium.

	Calculated for $ZrBr_4.4C_2H_5NH_2$.	Found.
Bromine	54·12	54·75
Zirconium	15·36	15·92
	Grm.	Grm.
Increase in weight	0·1098	0·1066

b. Thorium Tetrabromide, $ThBr_4.4C_2H_5NH_2$.—0·3121 grm. thorium tetrabromide, treated with ethylamine, gave 0·4098 grm. of a white compound which on analysis yielded:—

0·4246 grm. silver bromide = 0·1807 grm. bromine = 44·09 per cent bromine.

0·1502 grm. thorium dioxide = 0·1320 grm. thorium = 32·21 per cent thorium.

	Calculated for $ThBr_4.4C_2H_5NH_2$.	Found.
Bromine	43·71	44·09
Thorium	31·69	32·21
	Grm.	Grm.
Increase in weight	0·1018	0·0977

C. *Aniline.*

a. Zirconium Tetrabromide, $ZrBr_4.4C_6H_5NH_2$.—0·2075 grm. zirconium tetrabromide, treated with aniline, gave 0·4117 grm. of a brownish coloured compound which on analysis yielded:—

0·3821 grm. silver bromide = 0·1626 grm. bromine = 40·47 per cent bromine.

0·0631 grm. zirconium dioxide = 0·0467 grm. zirconium = 11·62 per cent zirconium.

	Calculated for $ZrBr_4.4C_6H_5NH_2$.	Found.
Bromine	40·83	40·47
Zirconium	11·46	11·62
	Grm.	Grm.
Increase in weight	0·1911	0·1932

b. Thorium Tetrabromide, $ThBr_4.4C_6H_5NH_2$.—0·2214 grm. thorium tetrabromide, treated with aniline, gave 0·3675 grm. of a brown coloured compound which on analysis yielded:—

0·3032 grm. silver bromide = 0·1290 grm. bromine = 35·10 per cent bromine.

0·1069 grm. thorium dioxide = 0·0939 grm. thorium = 25·56 per cent thorium.

	Calculated for $ThBr_4.4C_6H_5NH_2$.	Found.
Bromine	34·63	35·10
Thorium	25·11	25·56
	Grm.	Grm.
Increase in weight	0·1492	0·1461

D. *Pyridine.*

a. Zirconium Tetrabromide, $ZrBr_4.2C_5H_5N$.—0·3551 grm. zirconium tetrabromide, treated with pyridine, gave 0·3718 grm. of a brown compound which on analysis yielded:—

0·4876 grm. silver bromide = 0·2075 grm. bromine = 55·82 per cent bromine.

0·0802 grm. zirconium dioxide = 0·0604 grm. zirconium = 16·24 per cent zirconium.

	Calculated for $ZrBr_4.2C_5H_5N$.	Found.
Bromine	56·22	55·82
Zirconium	15·95	16·24
	Grm.	Grm.
Increase in weight	0·1357	0·1325

* Contribution from the John Harrison Laboratory of Chemistry. From the *Journal of the American Chemical Society*, xx, No. 11.

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b. Thorium Tetrabromide, $ThBr_4.C_5H_5N$.—0·2817 grm. thorium tetrabromide, treated with pyridine, gave 0·3343 grm. of a brownish compound which on analysis yielded:—

0·3960 grm. silver bromide = 0·1685 grm. bromine = 50·42 per cent bromine.

0·1412 grm. thorium dioxide = 0·1241 grm. thorium = 37·11 per cent thorium.

	Calculated for $ThBr_4.C_5H_5N$.	Found.
Bromine	50·71	50·42
Thorium	36·77	37·11
	Grm.	Grm.
Increase in weight	0·0403	0·0426

It will be noticed that these derivatives of the tetrabromides correspond very closely to those of the tetrachlorides of these same elements in the number of molecules of the amine in combination with one molecule of the halogen salt.

It may be remarked that Classen and Zahorski (*Zeit. Anorg. Chem.*, iv, 100) have obtained additive compounds of lead tetrabromide and lead tetraiodide with the hydrobromic and hydriodic acid salts of several of the organic amines, by decomposing the corresponding chlorine compounds with cooled solutions of potassium bromide or potassium iodide. Thus, $PbCl_4.2(C_9H_7N.HCl)$ with potassium bromide gave $PbBr_4.2(C_9H_7N.HBr)$, and with potassium iodide $PbI_4.2(C_9H_7N.HI)$.

PROCEEDINGS OF SOCIETIES.

CHEMICAL SOCIETY.

Ordinary Meeting, February 2nd, 1899.

Professor Dewar, F.R.S., President, in the Chair.

(Concluded from p. 81).

*17. "*The Chemistry of the so-called Nitrogen Iodide.*" Part I.—"*The Preparation and Properties of Nitrogen Iodide.*" By F. D. Chattaway and K. J. P. Orton.

Well-defined crystals of nitrogen iodide have been obtained by several new reactions. They are best produced by adding ammonia to a solution of potassium hypoiodite containing 0·02 grm.-molecule per litre. The liquid, after remaining clear for about half a minute, slowly deposits glittering needles, which are copper-coloured by reflected and red by transmitted light. These crystals have a specific gravity of 3·5, are dichroic, and probably belong to the orthorhombic system.

Part II.—"*The Action of Reducing Agents on Nitrogen Iodide.*" By F. D. Chattaway and H. P. Stevens.

All ordinary reducing agents rapidly decompose nitrogen iodide being themselves oxidised, whilst hydrogen iodide and ammonia are formed. The quantity of reducing agent oxidised is found in every case to be exactly double the amount equivalent to the hydrogen iodide produced.

The results obtained by the use of sodium sulphite, sulphurous acid, arsenious oxide, antimonious oxide, stannous chloride, and hydrogen sulphide are given in the following table:—

Amount of reducing agent oxidised:—	Na_2SO_3	H_2SO_3	As_2O_3	Sb_2O_3	$SnCl_2$	H_2S
Amount of hydriodic acid simultaneously produced—	HI	HI	2HI	2HI	HI	HI

The iodine contained in nitrogen iodide, therefore, behaves towards reducing agents like the chlorine contained in a hypochlorite, and exerts twice its normal oxidising action.

Part III.—"*The Composition of Nitrogen Iodide.*" By F. D. Chattaway.

Scarcely any of the numerous published analyses of nitrogen iodide agree, those of the same observer often differing widely. It is usually stated that a number of distinct compounds exist, but this statement is based entirely on these discordant results, and is unjustifiable, for in no case has the substance analysed been shown to be pure, and in no case has the reaction on which the analysis is based been thoroughly studied; two reactions, indeed, must always have occurred, one of which has been overlooked. A method of analysis has now been investigated, and the conditions necessary for a single reaction to take place determined. By means of this method, specimens prepared by every reaction known to yield nitrogen iodide have been analysed, weighed quantities of the dry substances being employed in all important cases.

It is thus proved that only one compound exists, and that this has a composition represented by the formula $N_2H_3I_3$. The molecular weight and the manner in which the atoms are linked together remain to be settled by further investigation.

Part IV.—"*The Action of Light on Nitrogen Iodide.*" By F. D. Chattaway and K. J. P. Orton.

Nitrogen iodide suspended in ammonia is decomposed both by sunlight and by artificial light, forming nitrogen and hydrogen iodide, the latter being neutralised by the ammonia, $N_2H_3I_3 = N_2 + 3HI$. At the same time, a very small quantity of the compound is hydrolysed, ammonia and ammonium hypoiodite being formed,—

$$N_2H_3I_3 + 3H_2O = 2NH_3 + 3HOI;\ 2NH_3 + 3HOI + NH_3 = 3NH_4OI.$$

The ammonium hypoiodite, being somewhat unstable, slowly changes into ammonium iodide and ammonium iodate, $3NH_4OI = 2NH_4I + NH_4IO_3$.

Similar actions take place when nitrogen iodide suspended in water is exposed to light, and further, the hypoiodous acid and a portion of the hydrogen iodide interact, with the result that nitrogen is evolved, and iodine, hydrogen iodide, and ammonium iodide are formed. Powdered iodine, when placed in ammonia and exposed to light, is partially converted into nitrogen iodide, which then reacts normally.

Part V.—"*The Action of Alkaline Hydrates, of Water, and of Hydrogen Peroxide on Nitrogen Iodide.*" By F. D. Chattaway and K. J. P. Orton,

Solutions of alkaline hydrates rapidly decompose nitrogen iodide, two reactions simultaneously occurring even when light is completely excluded.

The chief reaction is one of hydrolysis, ammonia and an alkaline hypoiodite being produced. These hypoiodites, however, are unstable, and more or less rapidly change into iodides and iodates. The equations representing the action of potassium hydroxide, for example, are—

$$N_2H_3I_3 + 3KOH = 2NH_3 + 3KOI = 2NH_3 + 2KI + KIO_3.$$

At the same time, a portion of the nitrogen iodide always breaks down exactly as under the influence of light (preceding abstract), yielding nitrogen and hydrogen iodide, which combines with the base forming the iodide. Solutions of ammonia or hydroxides of the alkaline earth metals act similarly.

Water causes an analogous decomposition, but in this case the hypoiodous acid formed in the hydrolysis decomposes the hydrogen iodide produced, liberating iodine. The action of water on nitrogen iodide is rendered more rapid by the presence of basic oxides, and of salts, such as iodides and carbonates, which can combine or react with the hypoiodous and hydriodic acids formed.

Hydrogen peroxide dissolved in a solution of potassium hydrate rapidly decomposes nitrogen iodide, ammonia, potassium iodide, and a trace of potassium iodate being produced, whilst oxygen mixed with a little nitrogen is

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evolved. The nitrogen iodide first reacts with the potash as if it alone were present, being hydrolysed to ammonia and potassium hypoiodite, but at the same time breaking down partially into nitrogen and hydrogen iodide. A very small quanity of the hypoiodite is transformed into iodide and iodate, but the greater part reacts with the hydrogen peroxide, liberating oxygen and being converted into iodide thus: $KOI+H_2O_2=KI+O_2+H_2O$. If a solution of hydrogen peroxide alone be added to nitrogen iodide, the water hydrolyses the compound and a similar action ensues, whilst iodine is set free by a further action of hydrogen peroxide on the hydrogen iodide remaining uncombined.

Part VI.—"*The Action of Acids on Nitrogen Iodide.*" By F. D. CHATTAWAY and H. P. STEVENS.

Dilute acids, when added to nitrogen iodide suspended in water, first induce hydrolysis of the compound, hypoiodous acid is liberated together with ammonia, which combines with the acid added—

$$N_2H_3I_3+\text{acid}+3H_2O=(2NH_3+\text{acid})+3HOI.$$

The further action depends on the nature of the acid used. If acids be employed such as sulphuric, phosphoric, boric, or acetic, on which hypoiodous acid has no effect, a rapid change into hydrogen iodide and iodic acid occurs, the former being immediately oxidised by a portion of the latter and iodine liberated,—

$$15HOI=10HI+5HIO_3=6I_2+6H_2O+3HIO_3.$$

If, however, the acid used reacts with hypoiodous acid, decomposition occurs, the nature of the final products depending on the acid employed. With hydriodic acid, for example, iodine is liberated, one half coming from the nitrogen iodide and one half from the acid,—

$$HOI+HI=I_2+H_2O;$$

with hydrochloric acid, iodine monochloride is produced: $HOI+HCl=ICl+H_2O$; whilst with hydrocyanic acid cyanogen iodide is formed, $HOI+HNC=INC+H_2O$.

In addition to this main action, it is found that when any acid except hydriodic or hydrocyanic acid is added to nitrogen iodide, light being excluded, a variable amount, depending on the strength of the acid, &c., decomposes exactly as it does under the influence of light, yielding nitrogen and hydrogen iodide; this hydrogen iodide then reacts with some of the hypoiodous acid formed in the hydrolysis, liberating iodine.

Part VII.—"*Theory of the Formation and Reactions of Nitrogen Iodide.*" By F. D. CHATTAWAY and K. J. P. ORTON.

In the formation of nitrogen iodide from iodine and aqueous ammonia, the iodine is first converted into equivalent quantities of ammonium iodide and ammonium hypoiodite, $I_2+2NH_4OH=NH_4I+NH_4OI+H_2O$; the greater part of the latter is then transformed into nitrogen iodide, which separates as a solid,—

$$3NH_4OI=N_2H_3I_3+NH_4OH+2H_2O,$$

but a small portion always remains unchanged. With iodine monochloride similar actions occur, ammonium chloride and hypoiodite being, however, the first products, $ICl+2NH_4OH=NH_4Cl+NH_4OI+H_2O$. If a solution of sodium or potassium hypoiodite be treated with a solution of ammonia, a partial conversion into the ammonium salt precedes the deposition of nitrogen iodide,—

$$KOI+NH_4OH=NH_4OI+KOH.$$

Solutions of ammonia kept in contact with nitrogen iodide are found to contain ammonium hypoiodite, the concentration increasing with the concentration of the ammonia and with the temperature. Nitrogen iodide is therefore formed from ammonium hypoiodite by a reversible action. This is found to be in accordance with the law of mass action if the concentration of the electrolytically dissociated ammonium hydroxide, NH_4OH, and not the total concentration of the ammonia, NH_3, be considered.

The experimental evidence so far seems to point to the conclusion that nitrogen iodide bears to ammonium hypoiodite a relation similar to that which the amide bears to the ammonium salt of an acid. The constitution of the compound, however, is still doubtful. The simplest explanation of its chemical behaviour is found in formulæ such as NH_3,NI_3 or NH_2I,NHI_2, whica represent each iodine atom as monovalent and direclly connected with nitrogen. It is certain that neither iodine nor hydrogen iodide is present in loose molecular combination such as occurs in periodides or acid iodides.

DISCUSSION.

Dr. ARMSTRONG pointed out that, from an indexer's point of view, it was most important not to multiply papers unduly, and expressed the opinion that the four papers submitted by Messrs. Chattaway and Orton should be entered under the one simple title, "Nitrogen Iodide"; only two entries would then be required, in place of eight, in the authors' index.

In view of Dr. Chattaway's explanation that the error in the analyses communicated in his previous paper was due to exposure to light, it was worth noting, perhaps, that chemists were not sufficiently careful in excluding light: for years past he had been in the habit of brominating benzenoid hydrocarbons in the photographic dark room, with the result that products were obtained which were entirely free from the irritating odour of benzyl derivatives, and might be taken into a drawing-room without hesitation.

Dr. SCOTT referred to the much larger yield obtained when the iodine employed was dissolved in a solution of potassium iodide, and asked whether the substance so prepared was free from potassium compounds, and, bearing in mind Bunsen's formula, NH_3,NI_3, for nitrogen iodide, whether it was not probable that some, or even the whole, of the NH_3 might be replaced by compounds such as KI, giving rise to substances such as KI,NI_3. He also pointed out that none of the reactions described by the authors accounted for the large quantity of iodine set free when nitrogen iodide was treated with water at a temperature of 50—60°, a process employed by Stas for the preparation of pure iodine in large quantity and with perfect safety.

The PRESIDENT remarked that Guyard had suggested the employment of nitrogen iodide as an actinometer, so that the decomposition in light had been observed already. This decomposition was interesting, as it led to the inference that the iodide was an endothermic substance.

Dr. CHATTAWAY, in reply, said that a full reference to Guyard's work was given in the paper. The authors were of opinion that they had settled finally the composition of nitrogen iodide, because every analysis made subsequent to the recognition of the causes of error confirmed it. The whole behaviour of the substance was in complete accord with this composition, and every reaction could be interpreted quantitatively.

The authors' results explained completely Stas's process for the purification of iodine. When nitrogen iodide is decomposed by water, two reactions had been shown to occur simultaneously and to an approximately equal extent: a part hydrolysed forming hypoiodous acid and ammonia, a part decomposed into hydrogen iodide and nitrogen, and the hydrogen iodide and hypoiodous acid interacted, liberating 90—95 per cent of the total iodine. Slight explosions, however, were always liable to occur, and the process consequently was dangerous. No evidence had been obtained of the existence of potassium compounds such as those suggested by Dr. Scott.

18. "*An Isomeride of Amarine.*" By H. LLOYD SNAPE, D.Sc., Ph.D., and ARTHUR BROOKE, Ph.D.

From the distillation products, and also from the mother-liquors obtained by the action of ammonium cyanide upon benzaldehyde, the authors have isolated a new base isomeric with amarine and melting at 198°. It

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forms salts with 1 equivalent of acids, forms a silver derivative containing 1 atomic proportion of the metal, and by distillation yields lophine.

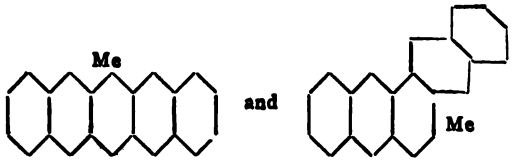
19. "*The Action of Chlorosulphonic Acid on Paraffins and other Hydrocarbons.*" By SYDNEY YOUNG, D.Sc., F.R.S.

In a paper by Dr. F. E. Francis and the author (*Trans.*, 1898, lxxiii., 932) it was shown that fuming nitric acid, at the temperature of a water-bath, acts far less energetically on normal paraffins than on iso-paraffins, methyl derivatives of the polymethylenes or aromatic hydrocarbons, and that, generally, the action is more rapid on hydrocarbons which contain a CH-group than on others.

Similar results have now been obtained with chlorosulphonic acid at the ordinary temperature, and it is shown that this reagent may be used for removing small quantities of isoparaffins and methyl derivatives of the polymethylenes from the normal paraffins separated from petroleum by fractional distillation.

29. "*Derivatives of Dibenzylmesitylene.*" By W. H. MILLS and THOMAS H. EASTERFIELD.

With the object of sythesising hydrocarbons of the types—



the authors have studied the benzoylation of mesitylene. Dibenzoylmesitylene has been described by Louise (*Ann. Chim. Phys.*, 1885, [vi.], vi., 191), but its isolation is difficult under the conditions employed by him. A good yield of the compound is obtained, however, by the interaction of benzoyl chloride with mesitylene at low temperatures in presence of much aluminium chloride. It is readily reduced by zinc dust and alcoholic potash, forming dihydroxydibenzylmesitylene, $C_6HMe_3(CHPh{\cdot}OH)_2$, a thick oil boiling at 326—330° at 50 m.m. pressure.

Dibenzylmesitylene is obtained from the secondary alcohol by prolonged reduction with zinc dust and alcoholic potash, or, more conveniently, by boiling with the diketone with hydriodic acid and phosphorus. Dibenzylmesitylene is sparingly soluble in cold, easily in hot alcohol, from which it crystallises in well-defined prisms. It melts at 89° and boils at 280° under a pressure of 30 m.m. Its vapour density agrees with that required for the formula $C_{23}H_{24}$. This dibenzylmesitylene differs from that described by Louise (*loc. cit.*), which melted at 131° and was sparingly soluble in hot alcohol. It is not improbable that the latter is a tribenzylmesitylene, and, as analysis alone cannot settle this point, Louise's experiments are being repeated.

When dibenzoylmesitylene is oxidised in sealed tubes with dilute nitric acid at 140°, it is almost completely converted into two isomeric *dibenzoyluvitic acids*; a small quantity of *dibenzoylmesitylenic* acid is formed at the same time. The latter may be precipitated from a solution of the mixed sodium salts and sodium acetate by dilute acetic acid, and the uvitic acids from the mother-liquor by hydrochloric acid. On treatment with methylic alcohol and hydrogen chloride, the crude dibenzoyluvitic acids yield two isomeric methylic salts. One of these is crystalline, melts at 248°, and is sparingly soluble in alcohol; the other is oily and easily soluble. On hydrolysis, the crystalline ethereal salt yields an acid melting at 262°; the isomeric acid from the oily salt melts at 210°. The acid of higher melting-point is the more easily etherified.

The mixture of dibenzoyluvitic acids is oxidised by alkaline permanganate to a *dibenzoyltrimesic* acid, which crystallises from dilute hydrochloric acid in minute rosettes melting at 245°. Its salts, with the exception of the silver, copper, lead, and ferric compounds, are easily soluble.

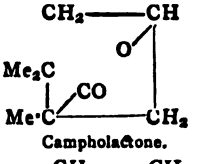
The action of condensing agents on these compounds is being investigated.

21. "*On Pseudocampholactone and Pseudolauronolic Acid.*" By FREDERICK H. LEES and W. H. PERKIN, Jun.

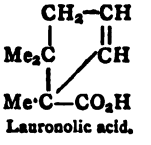
In a previous communication (*Proc.*, 1898, xiv., 111) the authors showed that, when camphoric anhydride is treated in chloroform solution with aluminium chloride at ordinary temperature, there is formed, besides isolauronolic acid, a new lactone, $C_9H_{14}O_2$, isomeric with campholactone and named pseudocampholactone. On hydrolysing this with baryta, a syrupy acid, $C_9H_{16}O_3$, was obtained; this eventually solidified, and has been found to consist of two isomeric acids, $C_9H_{16}O_3$, melting respectively at 109° and 152°.

Pseudocampholactone readily interacts with phosphorus pentabromide, and, on pouring the product into methylic alcohol, *methylic bromodihydro-ψ-lauronolate*, $C_8H_{14}Br{\cdot}CO_2Me$, is obtained; this boils at 160—165° at 35 m.m., and when digested with diethylaniline yields *methylic-ψ-lauronolate*, which boils at 212—213° at 751 m.m. pressure.

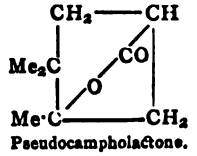
ψ-Lauronolic acid, $C_8H_{13}{\cdot}CO_2H$, obtained by hydrolysing its methylic salt, is a colourless oil boiling at 147—149° at 20 m.m.; it is slightly lævorotatory and is an unsaturated acid, as its solution in sodium carbonate instantly reduces permanganate. On digestion with 33 per cent. sulphuric acid, it is converted into pseudocampholactone. This new acid is of special interest, because it is isomeric with lauronolic, isolauronolic, campholytic, and allocampholytic acids, and the authors consider it probable that the relationship between campholactone and lauronolic acid, and pseudocampholactone and pseudolauronolic acid, may be represented by the formulæ—



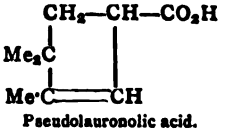
Campholactone.



Lauronolic acid.



Pseudocampholactone.



Pseudolauronolic acid.

Isolauronolic acid is not obtained when a solution of camphoric anhydride in chloroform is left in contact with aluminium chloride for several days, but in its place two new acids are formed—a crystalline saturated acid, $C_9H_{16}O_2$, melting at 76—77°, and a liquid unsaturated acid. These acids, as well as ψ-lauronolic acid, are being submitted to careful investigation, the results of which the authors hope soon to be able to communicate to the Society.

22. "*Nitrocamphor as an example of Dynamic Isomerism.*" By T. MARTIN LOWRY, B.Sc.

As has been pointed out in a previous communication (*Proc.*, 1898, xiv., 152), the rotatory power of both nitrocamphor and π-bromonitrocamphor varies, not only when different solvents are used, but also with time, and this may be regarded as proof that the normal and pseudo-forms of these substances are isodynamic, the change of structure being attended with a change of rotatory power in the freshly-prepared solutions. The change of rotatory power of nitrocamphor has been studied in fifteen different solvents; it usually extends over a period of a few hours or days, but at higher temperatures, or in presence of a trace of piperidine or of sodium ethylate, takes place

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almost instantaneously; on the other hand, a solution in chloroform can often be kept in a labile state during several days, which is perhaps an indication that the change is due to the presence of some third substance. Equilibrium is reached in the case of both nitrocamphor and π-bromonitrocamphor when about 6 per cent of the substance in solution is in the pseudo-form.

The author advances the opinion that the changes of rotatory power which take place in freshly-prepared solutions of many of the sugars are also due to the occurrence of isodynamic change, and not to the formation of hydrates, as has usually been assumed. In the case of glucose and of lactose, both isodynamic forms appear to have been isolated in an anhydrous state; when dissolved in water they pass to a condition of equilibrium in exactly the same manner as has been found to be the case with the isodynamic forms of π-bromonitrocamphor.

The bearing of the observations made with nitrocamphor on the general problem of dynamic isomerism is discussed in the concluding sections of the paper. The author hopes to extend this method of investigation to cyanocamphor and isonitrosocamphor, and to other optically active substances which may conceivably give rise to dynamic isomerides.

23. "*Position-isomerism and Optical Activity; the Methylic and Ethylic Salts of Benzoyl- and of Ortho-, Meta-, and Para-toluylmalic Acid.*" By Percy Frankland, F.R.S., and Frederick Malcolm Wharton.

In continuance of their work on the influence of position-isomerism on optical activity, the authors have prepared and examined the following compounds. The rotation of each compound was determined at temperatures ranging from 20—137°. The results may be summarised as follows (see Table).

Methylic Malate.

d	20°/4° = 1·2301	$[\alpha]_D$ 20°	= −6·84°

Methylic Benzoylmalate.

d	21°/4° = 1·2121	$[\alpha]_D$ 21°	= −5·62°
d	99°/4° = 1·1395	$[\alpha]_D$ 99°	= −11·56°
d	137·5°/4° = 1·1037	$[\alpha]_D$ 137·5°	= −13·64°

Methylic Orthololuylmalate.

d	23°/4° = 1·1909	$[\alpha]_D$	= −8·94°
d	98°/4° = 1·1181	$[\alpha]_D$ 98°	= −12·40°
d	135°/4° = 1·0822	$[\alpha]_D$ 135°	= −14·09°

Methylic Metatoluylmalate.

d	20°/4° = 1·1925	$[\alpha]_D$ 20°	= −6·34°
d	99°/4° = 1·1127	$[\alpha]_D$ 99°	= −11·73°
d	136°/4° = 1·0753	$[\alpha]_D$ 136°	= −13·49°

Methylic Paratoluylmalate.

d	18·5°/4° = 1·1957	$[\alpha]_D$ 18·5°	= −3·14°
d	99°/4° = 1·1088	$[\alpha]_D$ 99°	= −8·33°
d	136°/4° = 1·0688	$[\alpha]_D$ 136°	= −10·14°

Ethylic Malate.

d	20°/4° = 1·1340	$[\alpha]_D$ 20°	= −10·44°

Ethylic Benzoylmalate.

d	21°/4° = 1·1561	$[\alpha]_D$ 21°	= −3·87°
d	98°/4° = 1·0759	$[\alpha]_D$ 98°	= −9·84°
d	137°/4° = 1·0349	$[\alpha]_D$ 137°	= −12·08°

Ethylic Orthotoluylmalate.

d	21°/4° = 1·1391	$[\alpha]_D$ 21°	= −6·25°
d	100°/4° = 1·0714	$[\alpha]_D$ 100°	= −10·38°
d	136°/4° = 1·0405	$[\alpha]_D$ 136°	= −12·01°

Ethylic Metatoluylmalate.

d	21°/4° = 1·1371	$[\alpha]_D$ 21°	= −4·67°
d	99·5°/4° = 1·0603	$[\alpha]_D$ 99·5°	= −9·93°
d	137·5°/4° = 1·0229	$[\alpha]_D$ 137·5°	= −11·66°

Ethylic Paratoluylmalate.

d	20°/4° = 1·1382	$[\alpha]_D$ 20°	= −0·22°
d	99°/4° = 1·0513	$[\alpha]_D$ 99°	= −5·55°
d	136°/4° = 1·0106	$[\alpha]_D$ 136°	= −7·31°

Thus the lævorotation of ethylic malate is diminished by the introduction of all the acidyl groups in question. The lævorotation of methylic malate is also depressed by the introduction of the benzoyl, meta- and para-toluyl groups, but raised by that of the orthotoluyl group. At 20° the depressing, or dextrotatory, influence of the several groups follows in the order, para-toluyl > benzoyl > metatoluyl > orthotoluyl, both in the case of the methylic and ethylic compounds. At a high temperature (136°), on the other hand, the sequence of the dextrorotatory influences of these groups is parotoluyl > metatoluyl > benzoyl > orthotoluyl in the case of methylic malate, and paratoluyl > metatoluyl > orthotoluyl or benzoyl (practically identical) in the case of ethylic malate. In all cases, therefore, the dextrorotatory influence of the acidyl groups in question is more pronounced on the ethylic than on the methylic compound.

24. "*Some Regularities in the Rotatory Power of Homologous Series of Optically Active Compounds.*" By Percy Frankland, F.R.S.

The author endeavours to explain the results obtained in the previous paper (Percy Frankland and Wharton) by adducing evidence that methylic and ethylic malates both exist as associated molecules, and that methylic is more associated than ethylic malate. It is suggested that the lower lævorotation of methylic as compared with that of ethylic malate is due to the greater degree of association of the former, and that, in the unassociated state, the lævorotation of the methylic salt would be the greater. The acidyl-malates are probably much less, if not entirely, unassociated, hence the invariably greater lævorotation of the methylic acidyl-malate as compared with that of the corresponding ethylic derivative. The author reviews a large number of other homologous series of optically active compounds, and investigates the degree of association of each term with the aid of Traube's method of calculating molecular volume. From this investigation it would appear that the striking phenomenon of a maximum rotation occurring within an homologous series may probably be accounted for, in some cases, by the greater degree of association occurring in the initial terms, this association leading to the rotatory power actually observed being less than that possessed by the unassociated substance. In such cases, when a substitution is effected which does away with association, the maximum rotation within the series also disappears. Thus the malates exhibit a maximum rotation at the propylic term, whilst in the substituted malates the maximum disappears. In other cases the existence of a well-defined maximum rotation within an homologous series would not appear to admit of explanation in this manner. Such maxima occur in all well-authenticated cases at about the butylic term of the homologous series, and the author suggests that this may be due to stereochemical causes, as the occurrence of some irregularity in the rotation might be anticipated at the point where a growing chain attached to the asymmetric carbon atom attains such a magnitude that the chain has doubled on itself,—that is, when it contains about 5 carbon atoms. It is suggested that the same stereochemical cause may affect other physical properties, and that the greater tendency to association of the initial terms of an homologous series may be dependent on space conditions.

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25. "*On Brasilin and Hæmatoxylin.*" By A. W. GILBODY and W. H. PERKIN, Jun.

During the last three years the authors have been investigating these important natural colouring-matters, and now give a short abstract of the results obtained, in order that they may reserve the further study of the various decomposition products which they have prepared for the first time.

Trimethylbrasilin, $OH\cdot C_{16}H_{10}O(OME)_3$, when oxidised under certain conditions with chromic acid, yields *trimethylbrasilone*, $OH\cdot C_{16}H_8O_2(OMe)_3$, which crystallises in straw-coloured needles, melts at 191°, and at a somewhat higher temperature loses $1H_2O$, forming *dehydrotrimethylbrasilone*, $OH\cdot C_{16}H_6O(OMe)_3$. This crystallises in colourless needles, melts at 198°, and when treated with acetic anhydride is converted into an *acetyl* compound, $OAc\cdot C_{16}H_6O(OMe)_3$, which melts at 176°, and is probably identical with the substance which Herzig (*Monats.*, 1895, xvi., 913) obtained by oxidising acetyltrimethyl brasilin.

Nitric acid oxidises trimethylbrasilone, forming nitroparamethoxysalicyilc acid (m.p. 232°) and a substance represented probably by the formula $C_{11}H_8O_5(OMe)_2$; the latter crystallises in yellow needles, yields an acetyl compound, reacts with phenylhydrazine and parabromophenylhydrazine, and is characterised by forming an intense purple solution in dilute alkalis. If this purple solution is gently warmed dececomposition sets in, with the production of paramethoxysalicylic acid (m.p. 157°) and two neutral substances which melt at 118° and 206°, and which, on analysis, give numbers agreeing with those required for the formulæ $C_{11}H_{14}O_6$ and $C_{12}H_{14}O_6$ respectively.

From the mother-liquors obtained during the preparation of trimethylbrasilone the following substances have been isolated in small quantities:—(*a*) A substance crystallising in colourless needles and melting at 183°; this has not yet been analysed. (*b*) A substance crystallising in colourless crystals, melting at 210°, and giving with ferric chloride an intense violet colouration; the analysis gave numbers agreeing with those required for the formula $C_9H_{10}O_5$. (*c*) A substance melting at 155°, which crystallises from water in colourless needles, and appears to be a lactone of the formula $C_{15}H_{16}O_6$. This lactone, on oxidation with permanganate, yields a dibasic acid, $C_{10}H_{10}O_3(CO_2H)_2$, which melts at 200—203° with decomposition, due to the formation of the anhydride. When this dibasic acid is heated with hydrochloric acid at 160° it is decomposed with elimination of carbon dioxide, and, on extracting the solution with ether, beautiful colourless prisms are obtained, which melt at 104°, and consist of pure catechol; it thus appears probable that, in addition to the resorcinol ring, brasilin contains that of catechol.

When trimethylbrasilin is oxidised with permanganate it yields an acid melting at 129·5°, which apparently has the constitution $C_{10}H_8O_3(OMe)(CO_2H)$, and which, on fusion with potash, gives an oil which shows all the characteristic reactions of resorcinol. This acid, on oxidation with sodium hypobromite, is converted into an acid represented probably by the formula $C_{10}H_{10}O_9$, and this, on further oxidation with permanganate, gives an acid, $C_8H_8O_6$, which melts at about 225° with decomposition.

When *tetramethylhæmatoxylin*, $OH\cdot C_{16}H_9O(OMe)_4$ is oxidised with chromic acid, it yields *tetramethylhæmatoxylone*, $OH\cdot C_{16}H_9O_2(OMe)_4$, which melts at about 170° with decomposition. When heated with acetic anhydride it yields *acetyldehydrotetramethylhæmatoxylone*,—

$$OAc\cdot C_{16}H_5O(OMe)_4,$$

which crystallises in colourless needles, melts at 194°, and is probably identical with a compound melting at 191—192°, which Herzig (*loc. cit.*) obtained by oxidising acetyltetramethylhæmatoxylin.

When oxidised with nitric acid tetramethylhæmatoxylone behaves in the same way as trimethylbrasilone, yielding a substance which crystallises in yellow needles, and dissolves in alkalis with a purple colour. This substance is being investigated, as also are several substances which have been obtained from the mother-liquors obtained during the preparation of tetramethylhæmatoxylone. One of the latter compounds crystallises from water in colourless needles, melts at 214°, and on analysis gives numbers agreeing with those required for the formula $C_9H_{10}O_3(CO_2H)_2$.

The authors hope, by the examination of all these new substances, to obtain results which will enable them to assign formulæ to brasilin and hæmatoxylin, and they are continuing the investigation with the aid of Mr. H. Hibbert, B.Sc., who has already afforded much assistance in examining tetramethylhæmatoxylone.

NOTICES OF BOOKS.

Physico-Chemical Methods. By Dr. J. TRAUBE, Privat Docent in the Technical High School of Berlin. Authorised Translation by WILLITT L. HARDIN, Ph.D., Harrison Senior Fellow in Chemistry, University of Pennsylvania. Philadelphia: P. Blakiston's Son and Co. London: Kegan Paul, Trench, Trübner, and Co., Lim.

FULLY recognising the importance of physico-chemical methods in chemical investigation, we are glad to see an English translation of this important work.

The book opens in the usual way by a description of the balance, and rules for adjusting and working with it. Methods for estimating the density of solids, liquids, and gases are given at length, including descriptions and illustrations of most of the standard forms of apparatus for this purpose; in fact, the book is really a compilation of the various forms of apparatus for physico-chemical analysis at present in use in Continential laboratories.

The illustrations are poor, and in some cases very bad (see p. 65, "The Thermostat").

The translator in some instances has scarcely done justice to the work, and some of the expressions used are open to criticism. On page 15 a ground glass stopper is twice called a *cork*. In another place reference is made to an "everywhere purchaseable turbine"; this being the only description of the apparatus. And in another place, in describing the adjustment of the Hüfner-Albrecht rhomb in the spectrophotometer, we are told that a prism is to be *shoved* into its place!

A passage, too, on page 77 giving the method of filling a pycnometer with mercury in determining the coefficient of expansion is very indifferently translated, and reads:—"By carefully heating and cooling the pycnometer whereby the mercury is slowly heated to boiling the vessel is completely filled."

These oversights, trivial though they appear, detract much from the value of the book.

Notes on Essential Oils. With Special reference to their Composition, Chemistry, and Analysis. By T. H. W. IDRIS, F.C.S. With Tables of Constants of the more commonly occurring Oils. London and Bristol: Geo, Du Boistel and Co.

THIS little book will be found of great practical value to those working in essential oils. Not intended as a text-book, the details of analytical processes are omitted, but at the same time much practical information is given that is not at all likely to be found in an ordinary text-book.

In Chapter I., dealing with the camphor group, the obscurity of the chemistry of this group of compounds is pointed out, but a good outline of the most trustworthy data is given from the works of Bredt, Tiemann, Perkin, and others.

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In the essential oils, the increasingly important oil of eucalyptus is briefly but clearly described, and some practical notes on methods of analysis are given, concluding with a table of specific gravity, optical rotation, and constituents of the oils from some fourteen species of eucalyptus.

The book concludes with a Table of Constants, giving the source, specific gravity, optical rotation, &c., of essential oils arranged in alphabetical order.

There is a clearly printed table of contents, enabling the data of any oil to be found with a minimum amount of labour.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

NOTE.—All degrees of temperature are Centigrade unless otherwise expressed.

Comptes Rendus Hebdomadaires des Séances, de l'Académie des Sciences. Vol. cxxviii., No. 2, January 9, 1899.

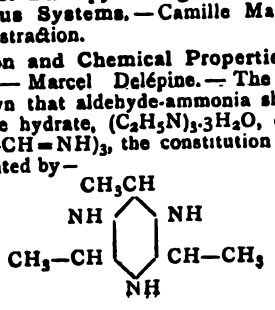
Preparation and Properties of Calcium Arsenide.—P. Lebeau.—The author has prepared in the electric furnace a crystallised arsenide of calcium with the formula As_2Ca_3, corresponding to the nitride N_2Ca_3. As in the case of the nitride and phosphide of calcium this arsenide decomposes water at ordinary temperatures, giving a gaseous hydride of formula AsH_3 and calcium hydrate. The arsenide prepared by the direct union of calcium and arsenic has exactly the same composition.

Decomposition of Carbonic Oxide in presence of Iron Oxide.—O. Boudouard.—The author's experiments show that the reaction of decomposition of carbonic oxide is a function of the time, and that it depends also on the quantity of iron oxide present. The amount of carbonic acid formed increases in a regular manner, and the decomposition ends by being total in the first two series of experiments, and no doubt the same result would be obtained in the third at the end of a sufficiently long time. The author investigates also the action of carbonic oxide in the presence of nickel and cobalt oxides at the same temperature of 445° and also at higher temperatures.

Volumetric Estimation of Cerium.—André Job.—A known weight of ammonium cerium nitrate is dissolved in nitric acid. The amount of oxide present per unit volume can be found by calcination. Dilute standard peroxide of hydrogen solution is run in until the nitrate is completely decolourised. By this means the amount of ceric cerium in acid solution can be estimated. From this the author deduces a method of estimating the total cerium present. He treats the cerium salt with binoxide of lead in the cold in presence of excess of nitric acid. The cerous salt is oxidised to ceric, and can be estimated volumetrically by the former method. This estimation can take place in the presence of thorium, lanthanum, and didymium.

Variation of Entropy during the Dissociation of Heterogeneous Systems.—Camille Matignon.—Not suitable for abstraction.

Constitution and Chemical Properties of Ethylidene-imine.—Marcel Delépine.—The author has formerly shown that aldehyde-ammonia should be considered as the hydrate, $(C_2H_5N)_3.3H_2O$, of ethylidene-imine, $(CH_3—CH=NH)_3$, the constitution of the latter being represented by—



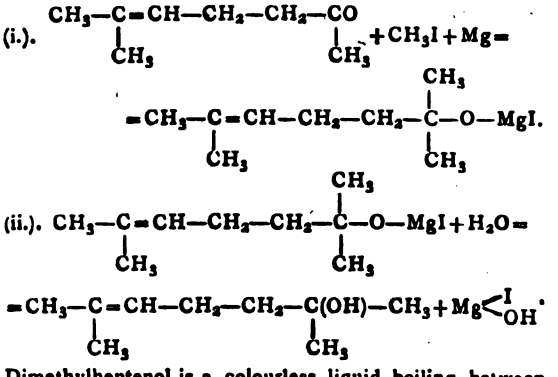
Facts are deduced in support of this formula. (1) The aldehyde-ammonia is a hydrate; ethylidene-imine being obtained from it when dried *in vacuo* over H_2SO_4. (2) One CH_3CH is joined to two N, as shown by the production of the body—

$$CH_3—CH<\begin{matrix}NH.CO.C_6H_5\\NH.CO.C_6H_5\end{matrix}$$

when benzoyl chloride reacts with aldehyde-ammonia (3) The substance reacts as a secondary amine. (4) The molecule has a chain of six links.

Derivatives of Synthetic Methylheptenone.—Georges Leser.—The method of preparation of the ethyl ester of methylhexenone-pyruvic acid has been described. The corresponding acid is obtained by the action of sodium ethylate on methylheptenone and oxalic ether. The new acid is isolated, by precipitating with hydrochloric acid, in the form of colourless prisms melting at 39—50°, very soluble in most organic solvents. Analysis agrees with the formula $C_{10}H_{14}O_4$.

Synthesis of Dimethylheptenol.—Ph. Barbier.—One hundred grs. of natural methylheptenone, 150 grs. of anhydrous ether, and 20 grs. of magnesium turnings are placed in a flask, and 113 grs. of methyl iodide gradually added. The reaction is brisk, and the flask is cooled by a current of water. On addition of sulphuric acid, a liquid separates which is fractionated *in vacuo*. The reaction is represented as follows:—



Dimethylheptenol is a colourless liquid boiling between 79—80° under 10 m.m.

A Method of Formation of Urea.—A. Jouve.—The author has proved that a solution of carbon monoxide in ammoniacal cuprous chloride warmed to 105° for five or six hours gives urea. The reaction is expressed thus:—

$$(i.).\quad CO+(NH_2)_2=CO<\begin{matrix}NH_2\\NH_2\end{matrix}+H_2,$$

$$(ii.).\quad Cu_2Cl_2+H_2=2HCl+Cu_2;$$

for, on the one hand, copper is deposited, and, on the other hand, the weight of metal formed and the weight of urea estimated by hypobromite are in the ratio indicated by these equations. The fatty and aromatic amines behave in an analogous manner. By dissolving cuprous chloride in dimethylamine and reacting with CO under pressure copper is formed, and probably also a urea; this has not yet been isolated.

MISCELLANEOUS.

On the Use of Acetylene as a Reagent in Quantitative Analysis.—H. G. Söderbaum.—*The Separation of Copper and Cadmium.*—The mixture of the two salts (0·5 to 0·8 grm.) is dissolved in about 150 cubic c.m. of water; 10 to 15 cubic c.m. of sulphurous and 20 to 25 cubic c.m. of ammonia of sp. gr. 0·96 are added. The solution is heated on the water-bath until it takes a

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bright blue colour, and is then treated with a current of acetylene. The precipitate is washed several times by decantation with dilute ammonia saturated with acetylene, thrown on a filter, and washed with boiling water. The acetylide of copper thus obtained is heated with nitric acid, and the resulting nitrate is transformed into oxide by calcination, and then weighed. In the solution freed from acetylide of copper the cadmium is precipitated by ammonium sulphydrate, or else determined electrically after acidulation, and heating to drive off the sulphurous acid. *Separation of Copper and Arsenic.*—If the arsenious or arsenic acid is in the form of an ammoniacal salt, the separation of the copper in the state of acetylide is incomplete, the precipitate always carrying down with it a certain proportion of arsenic. This inconvenience can be remedied by adding to the liquid a quantity of caustic soda sufficient to saturate the arsenious or arsenic acid. A current of acetylene is passed through the warm solution, until the precipitate collects easily and the liquid becomes clear. The filtrate is evaporated to dryness, the residue oxidised by nitric acid, and the resulting solution precipitated by magnesia mixture in the ordinary manner. The acetylene used in these operations should be washed with acetate of lead and acid bichloride of mercury; the object of using this latter is to absorb the phosphoretted hydrogen. In some experiments, when the acetylene was not washed with bichloride of mercury, the precipitate of acetylide of copper contained traces of phosphorus.—*Berichte*, xxx. [9], p. 3014.

NOTES AND QUERIES.

*** Our Notes and Queries column was opened for the purpose of giving and obtaining information likely to be of use to our readers generally. We cannot undertake to let this column be the means of transmitting merely private information, or such trade notices as should legitimately come in the advertisement columns.

Glass Specimen Bottles.—I shall be obliged if any reader of the CHEMICAL NEWS will inform me where stoppered bottles with feet can be obtained. They are, I believe, called "Roscoe" bottles.—W. C.

MEETINGS FOR THE WEEK.

MONDAY, 27th.—Society of Arts, 8 (Cantor Lectures). "Cycle Construction and Design," by Archibald Sharpe, A.M.Inst.C.E.

TUESDAY, 28th.—Royal Institution, 3. "The Morphology of the Mollusca," by Prof. E. Ray Lankester, M.A., LL.D.

—— Society of Arts, 8. "Persian Trade Routes," by A. Hotz.

WEDNESDAY, March 1st.—Society of Arts, 8. "Leadless Glazes," by Wilton P. Rix.

THURSDAY, 2nd.—Royal Institution, 3. "Toxins and Antitoxins," by Dr. Allan Macfadyen, M.R.C.S.

—— Chemical, 8. "Brom-methylfurfuraldehyde," by H. J. H. Fenton and Mildred Gostling. B.Sc. "The Action of Metallic Thiocyanates on certain Substituted Carbamic and Oxamic Chlorides—and a New Method for the Production of Thiobiurets," by A. E. Dixon, M.D. "Ethylic $\beta\beta$-Dimethylpropanetetracarboxylate," by W. Trevor Lawrence. "The Reaction of Alkyl Iodides with Hydroxylamine—Formation of Alkylated Hydroxylamines and Oxamines," by Wyndham R. Dunstan, F.R.S., and John Goulding, B.Sc.

FRIDAY, 24th.—Royal Institution, 9. "King Alfred," by Sir Frederick Pollock, Bart., M.A., LL.D.

SATURDAY, 4th.—Royal Institution, 3. "The Mechanical Properties of Bodies," by The Right Hon. Lord Rayleigh, F.R.S., &c.

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Offices of the Drainage Board, Engineer to the Board.
Council House, Birmingham,
February 14th, 1899.

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THE CHEMICAL NEWS.

Vol. LXXIX., No. 2049.

THE FORMATION OF PERCHLORATES OF THE ALKALIS, AND OF THE ALKALINE EARTHS, BY ELECTROLYSIS.

By F. WINTELER.

The prolonged electrolysis of the alkaline chlorides or of the alkaline earths in aqueous solution with platinum electrodes may give rise to the formation, not only of hypochlorites and chlorates, but also to that of perchlorates. In the short accounts which have already been published on the electrolytic transformation of chlorate of potassium into the perchlorate by means of platinum electrodes it is the more singular that none of the patents having for their object the electrolytic manufacture of chlorates take any notice of this phenomenon, and that the works quoted (Gmelin-Kraus "Handbuch d. Anorg. Chem.," I. *a.*, p. 696; I. *b.*, p. 373; II. *a.*, p. 80; Gilbert's *Ann. Phys.*, 1816, lii., p. 218-219; *Journ. Prakt. Chem.*, 1847, xli., p. 138-139), have not been reproduced in any modern text-books.

When the electrolysis of the solutions of chlorides between the platinum electrodes has arrived at such a point that all the chloride is transformed into chlorate, the best conditions for the further oxidation of the chlorate into perchlorate are:—

1. The solution must be acid at the anode.
2. The temperature must be low at the anode.
3. The density of the current should be from 4 to 12 ampères per square decimetre.
4. The electrolyte should be a saturated solution.

If, for example, we electrolyse, without a diaphragm, a neutral solution of chlorate of potassium saturated at the ordinary temperature, with 8 ampères per square decimetre, taking care to maintain the temperature of the bath at 10° by means of a current of water, we find that at the commencement 73 per cent of the oxygen which should be disengaged is utilised in transforming the chlorate into perchlorate. A saturated solution of chlorate of sodium 1:1 gives under the same circumstances perchlorate of sodium with a return of 95 per cent. The return only commences to diminish at the moment when the chlorate is almost entirely oxidised; it then diminishes very rapidly.

It is of importance to cool the electrodes immediately. The apparatus should be constructed in such a manner that the electrodes are in contact with the electrolyte on one side only, otherwise the density of the current cannot be accurately measured. If, however, this condition cannot be fulfilled, the side of the anode facing the cathode is practically all that need be considered. The density of the current at the cathode may be arranged as we like, as it has no effect on the electromotive force of the current.

Reduction of the chlorate does not take place at all, even when we have to deal with a very feeble current. All conditions being equal, the best return is obtained with a current of from 8 to 12 ampères per square decimetre of the anode. The return is lowered if the density of the current is increased or diminished. Even solutions of chlorates containing 4 per cent of alkali furnish corresponding perchlorates, giving a return up to 10 per cent if the electrolyte at the anode and at the cathode is not disturbed except by the gas which is given off.

The formation of perchlorates is accompanied by the characteristic smell of ozone. A concentrated solution of chlorate and perchlorate gives off such large quantities of ozone that the indiarubber tubes and joints are reddened after only a few minutes. It would be worth while to carry out a research in this direction, with the object of preparing ozone industrially by means of electrolysis.

If carbon be used as the anode for the electrolysis of the chlorate, it is used up very rapidly without the formation of any perchlorate. The use of other metals than platinum and iridium is impossible on account of the formation of soluble salts with the anion ClO_3.

An interesting observation made by Riche (*Comptes Rendus*, 1858, p. 348), and which of late years has passed unnoticed, is one relating to the formation of perchloric acid by the electrolysis of dilute hydrochloric acid between two platinum electrodes. According to my own experiments the most favourable conditions for this reaction are the same as those for the electrolytic preparation of the perchlorates. We obtain an acid the more concentrated as the temperature of the bath is lower. The temperature at which the chlorine remains entirely in solution is the most favourable.—*Chemiker Zeitung*, 1898, xxii., p. 90.

ON THE SEPARATION OF IRON FROM ZIRCONIUM AND CERTAIN OTHER ALLIED METALS.*

By J. MERRITT MATTHEWS.

Though there have been several methods proposed in the past for the separation of iron from zirconium, still chemists have not considered that this problem has, as yet, been satisfactorily solved. All methods which have been recommended for the quantitative separation of these two metals have proved, in some particular, to be untrustworthy, for in all of them traces of iron appear to remain with the zirconium with great pertinacity.

As it may be of interest in connection with the present subject, a brief résumé will here be given of the principal metnods which have hitherto been proposed for the separation of iron from zirconium.

Bailey (*Journ. Chem. Soc.*, xlix., 481), by the use of a moderately concentrated solution of hydrogen peroxide, precipitates Zr_2O_5, whereas neither iron, aluminum, nor titanium salts are precipitated by this reagent. No accurate results, however, have been worked out by this method.

Berlin (*Journ. Prakt. Chem.*, lviii., 147), observes that if zirconium dioxide, contaminated with iron, is fused with sodium carbonate to a white heat, and the fusion treated with hydrochloric acid, the iron salt dissolves, leaving the zirconium dioxide undissolved. Scheerer (*Pogg. Ann.*, lix., 48), claims that by this fusion a sodium zirconate is formed at first, which is subsequently decomposed on washing with water. Some of the zirconium, however, will go into the solution with the iron; and, on the other hand, the zirconate dioxide will still be slightly contaminated with traces of ferric oxide.

Stromeyer (*Ann. Chem. Pharm.*, cxiii., 127), applies Chancel's method (*Journ. Prakt. Chem.*, lxxiv., 471), for the separation of iron from aluminum to its separation from zirconium. By boiling with sodium thiosulphate, zirconium hydroxide is precipitated, while the iron remains in solution. Hermann (*J. Pr. Chem.*, xcvii., 340), however, says that this procedure results in the formation of a zirconium hyposulphite; and traces of iron still continue with the zirconium. For an approximate separation, however, this seems to be a good one.

Rivot (*Ann. Chim. Phys.*, xvii., 244), recommends the reduction of the iron to the metallic condition, by heating in a current of hydrogen. But it is very doubtful if all of the iron will be eliminated from the zirconium dioxide by this means.

* *Journal of the American Chemical Society*, xx., No. 11, Nov., 1898.

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Berthier (*Ann. Chem. Phys.*, l., 362), uses ammonium hydroxide and sulphide, which precipitates ferrous sulphide, FeS, and zirconium hydroxide, $Zr(OH)_4$; when this mixture is treated with sulphurous acid, the ferrous sulphide dissolves; the filtrate may contain some zirconium salt which, on heating, is precipitated from the iron as hydroxide. Hermann claims that this method does not give zirconium dioxide free from iron. Henneberg (*Journ. Prakt. Chem.*, xxxviii., 508), obtains a zirconium dioxide pure, except in that portion which is precipitated on heating.

Hermann claims to have obtained very pure zirconium dioxide by treating a solution of the chloride with a corresponding amount of ammonium oxalate, and igniting the precipitate. But in this method the amount of zirconium must be known beforehand, in order to calculate the quantity of ammonium oxalate to be added, as any excess of the latter reagent will dissolve the precipitate.

Dubois and Silveria observe that if impure zirconium hydroxide is boiled with oxalic acid, the iron oxalate formed is easily soluble, whereas the zirconium oxalate is insoluble. But Berlin (*Journ. Prakt. Chem.*, lviii., 145), found that the zirconium oxalate is somewhat soluble in oxalic acid, which fact vitiates this method.

Classen (*Ber. d. Chem. Ges.*, xiv., 2783), gives an electrolytic separation of iron from zirconium; but by his method the zirconium is only determined by difference.

Another method which has been recommended is to boil the impure zirconium salt with a solution of potassium sulphate, when a basic sulphate of zirconium will be precipitated. The precipitation, however, is never comcomplete, as the filtrate always contains some of the zirconium.

It will be seen by this short review that the separation of iron from zirconium is by no means a positive certainty, as there seems to be a great many conflicting opinions entertained by the different authorities.

Details of the Method for the Separation of Iron from Zirconium.

On introducing a small quantity of water into an ethereal solution of zirconium tetrachloride, it was noticed that a white precipitate was formed, insoluble in excess of ether. This precipitate was no doubt an oxychloride of zirconium, and analysed in accordance with the well-known hydrated chloride, $ZrOCl_2 \cdot 8H_2O$.

I. 0·1682 grm. material gave:—

0·1492 grm. silver chloride = 21·93 per cent chlorine.

0·0645 grm. zirconium dioxide = 28·34 per cent zirconium.

II. 0·1276 grm. material gave:—

0·1181 grm. silver chloride = 21·86 per cent chlorine.

0·0488 grm. zirconium dioxide = 28·26 per cent zirconium.

	Calculated for $ZrOCl_2 \cdot 8H_2O$.	Found. I.	Found. II.
Chlorine	22·05	21·93	21·86
Zirconium	28·18	28·34	28·26

On testing this precipitate with a solution of potassium thiocyanate, not a trace of iron was indicated, although the zirconium tetrachloride used in the solution showed a decided contamination by iron under the same conditions.

With this sharp distinction in solubilities of the hydrated salts of zirconium and iron in ether as a basis, a simple and accurate separation of these two elements was immediately suggested.

Weighed quantities of the chlorides of zirconium and iron were mixed together. Previous analyses of these salts were made in order to determine their respective percentages of zirconium and iron. The mixed salts were dissolved in water and carefully evaporated to dryness on a water-bath; after cooling they were treated with absolute ether, and dry hydrochloric acid gas was passed through the liquid. Experience proved that this latter treatment was necessary to effect a rapid and complete solution of the iron salt by the ether, as the ferric chloride on evaporation to dryness evidently forms basic compounds of indefinite composition which are difficulty soluble in ether. The solution was rapidly filtered, and the residue washed with absolute ether several times to insure the removal of the last traces of the iron salt. The residue was then dissolved in water, and the zirconium determined by precipitation as hydroxide by means of ammonium hydroxide; drying the precipitate, igniting and weighing as zirconium dioxide, ZrO_2. The ether was evaporated or distilled from the filtrate, and the residue dissolved in water, with the addition of a few drops of hydrochloric acid if necessary; and the iron was determined by precipitation with ammonium hydroxide, drying the precipitate, igniting, and weighing as ferric oxide, Fe_2O_3.

On testing the aqueous solution of the residue containing the zirconium with potassium thiocyanate solution, not a trace of iron was discovered, showing that the separation had been a complete and successful one.

Several analyses were made, using varying relative amounts of the zirconium and iron salts.

I. 0·1824 grm. ferric chloride with 0·1262 grm. zirconium tetrachloride gave:—

0·0540 grm. ferric oxide = 29·50 per cent ferric oxide.

0·0615 grm. zirconium dioxide = 48·89 per cent zirconium dioxide.

II. 0·1763 grm. ferric chloride with 0·1890 grm. zirconium tetrachloride gave:—

0·0524 grm. ferric oxide = 29·55 per cent ferric oxide.

0·0920 grm. zirconium dioxide = 48·83 per cent zirconium dioxide.

III. 0·3064 grm. ferric chloride with 0·1620 grm. zirconium tetrachloride gave:—

0·0910 grm. ferric oxide = 29·60 per cent ferric oxide.

0·0788 grm. zirconium dioxide = 48·79 per cent zirconium dioxide.

IV. 0·6564 grm. ferric chloride with 0·2544 grm. zirconium tetrachloride gave:—

0·1931 grm. ferric oxide = 29·36 per cent ferric oxide.

0·1240 grm. zirconium dioxide = 48·78 per cent zirconium dioxide.

V. 0·1276 grm. ferric chloride with 0·6924 grm. zirconium tetrachloride gave:—

0·0390 grm. ferric oxide = 29·70 per cent ferric oxide.

0·3385 grm. zirconium dioxide = 49·04 per cent zirconium dioxide.

On analysing the ferric chloride used it gave 29·44 per cent ferric oxide, while the zirconium chloride gave 48·97 per cent zirconium dioxide. The latter salt also showed a contamination by iron equivalent to 0·16 per cent ferric oxide, and in the percentages given in the above analyses, an allowance is made for this correction.

	Used.	Found. I.	II.	III.	IV.	V.
Ferric oxide	29·44	29·50	29·55	29·60	29·36	29·70
Zirconium dioxide..	48·97	48·89	48·83	48·79	48·78	49·04

In making a practical use of this separation it is only necessary to obtain the two metals in solution in the form of chlorides and then the details as already given may be applied.

On the Delicacy of the Separation of Iron from Zirconium.

The fact that zirconium oxychloride is perfectly white in colour should not be taken as a final indication that it is absolutely free from traces of iron; and this should be borne in mind in the preparation of salts for atomic weight determinations. In order to establish the accuracy of the method which has been described for the separation of iron from zirconium, a series of delicate experiments was carried out with the object of determining approximately the quantity, if any, of iron still remaining with the zirconium salt.

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Zirconium tetrachloride, contaminated with iron, was treated with a little water in order to convert it into the oxchloride; it was then digested with ether, and a drop of hydrochloric acid added. The ether was filtered off and the perfectly white residue of zirconium oxychloride was washed several times with absolute ether to ensure the removal of the last traces of the iron salt.

A solution of ferric chloride was made, one c.c. of which contained 0·000001 grm. ferric chloride. This was called solution No. 1.

Another solution of ferric chloride was made, one c.c. of which contained 0·0000005 grm. ferric chloride. This was called solution No. 2.

One c.c. of solution No. 1 was placed in a test-tube, and to this were adeed one c.c. of hydrochloric acid (sp. gr. 1·17), and one c.c. of a solution of 10 grms. ammonium thiocyanate in 100 c.c. of water, and the volume of the liquid was made up to 10 c.c. A slight pink colour was noticed. One c.c. of solution No. 2 was treated in the same manner, and a just perceptible pink tinge was observed.

One-tenth grm. of zirconium tetrachloride was dissolved in 5 c.c. of water, and treated as above; a dark red colour immediately appeared.

One-tenth grm. of the zirconium oxychloride as freed from iron was dissolved in 5 c.c. of water, and treated in a similar manner; a very slight pink tinge was perceptible. On comparing this with solutions No. 1 and No. 2, it was found that the intensity of colouration of the zirconium oxychloride solution was between that of the two iron solutions. From this it is to be concluded that the ratio between the amount of iron salt and that of the zirconium salt present in the zirconium oxychloride is approximately between the limits of 1 : 200,000 and 1 : 100,000.

The tetrachloride of zirconium, before its separation from iron, showed a percentage of the latter equivalent to about 0·16 per cent ferric oxide. By the above comparison this percentage appears to be reduced to something approximately between the limits of 0·001 and 0·0005 per cent. The solution of hydrochloric acid used in these experiments was purified to such an extent that 1 c.c., when treated with 1 c.c. of the ammonium thiocyanate solution, on dilution to 10 c.c. gave no perceptible pink colouration.

The observations of those delicate tints were made immediately after mixing the solutions, and by comparison with an equal volume of distilled water. On standing for a time the colours were apparently discharged.

(To be continued).

THE ESTIMATION OF BORIC ACID.*

By F. A. GOOCH AND LOUIS CLEVELAND JONES.

The estimation of boric acid by treating the salts of that acid with sulphuric acid, distilling with methyl alcohol, evaporating the distillate over magnesium oxide, igniting and weighing, was proposed by Rosenbladt (*Zeitschr. für Anal. Chem.*, xxvi., 21). A little later, and without knowledge of Rosenbladt's experience, a somewhat similar process (*Am. Chem. Journ.*, ix., 23), which consisted in the treating of the compound of boric acid with acetic acid or nitric acid, distillation with methyl alcohol, evaporation of the distillate over calcium oxide, and ignition of the residue, was described by one of us. In the course of the development of this process, it transpired that the insolubility of magnesium oxide retards the absorption of boric acid by that substance, and that the more soluble calcium oxide retains boric acid more actively and is therefore to be preferred.

Points in the treatment upon which special emphasis was laid in the original description of this process were the choice of a suitable apparatus for the distillation, the employment of a loosely stoppered receiver for the reception of the distillate upon slaked lime, the careful removal of water from the substance in the retort before acidifying and treating with the methyl alcohol, regulated use of acid, and care in the evaporation and ignition.

The attainment of good results in this process depends upon attention to details. Modifications have been suggested by several investigators. Thus, instead of igniting the calcium oxide in a large platinum crucible, transferring it to the receiver to hold the boric acid, and returning the calcium oxide with the distillate to the same crucible for subsequent ignition of the residue, as was originally proposed, Penfield (*Am. Journ. Sci.*, xxxiv., 222), prefers to ignite the calcium oxide in a small crucible, to collect the distillate in ammoniacal water, to evaporate the latter over the calcium oxide in a large platinum dish, and to transfer this residue back to the small crucible for the final evaporation and ignition. Kraut (*Zeitschr. für Anal. Chem.*, xxxvi, 3), suggests a modification of form in the apparatus with no other essential change in conditions. Moissan (*Comptes Rendus*, cxvi., 1084), has suggested changes in the apparatus and avoids a transfer of the calcium oxide—collecting the distillate by itself in a closed receiver, trapped with an ammonia bulb to prevent the escape of the boric acid from the distillate. Furthermore, Moissan's process calls for the use of an amount of calcium oxide from fifteen to twenty times greater than that theoretically required. From our experience it seems obvious that the demand for this amount of calcium oxide arises from an excessive use of nitric acid in the retort and the consequent modification of conditions in the distillate. Fortunately this difficulty may be avoided by the use of a little phenolphthalein as an indicator in the retort and care to limit the addition of nitric acid to the amount required to produce distinct acidity. The addition of a drop of the acid and another of the indicator should be repeated once or twice during the distillation to insure the replacement of the acid volatilised from the salt slightly decomposed in the process. The effect of much nitric acid is bad, not only because it neutralises the calcium oxide when it passes to the distillate, but because when it is used a tendency is developed on the part of the dried mixture of calcium hydroxide and borate to puff explosively if this ignition is begun as soon as the residue is dry. If the residue is heated gradually and as strongly as possible over a radiator before the flame is actually applied to the crucible, no such action takes place; we are disposed to attribute it to the effect of the nitrate and nitrite, produced by the absorption of nitrous fumes in the lime, upon the alcohol or other organic matter retained by the lime in the evaporation and drying unless the latter process is prolonged at high temperature.

That good results may be obtained with small amounts of calcium oxide provided care as to the use of nitric acid and the conditions of ignition be taken, is shown by the figures of the original description and by the following experiments, in which phenolphthalein was employed as an indicator and the residue heated strongly over the radiator before actual ignition.

CaO taken. Grm.	B_2O_3 taken. Grm.	B_2O_3 found. Grm.	Error. Grm.
2·3405	0·1788	0·1792	+0·0004
1·7620	0·1790	0·1785	—0·0005
2·1757	0·1824	0·1840	+0·0016
2·5656	0·1788	0·1786	—0·0002

These results are accurate within reasonable limits. On the other hand, without care to ignite gradually we have noted errors of from 0·0030 grm. to 0·0060 grm. in the process otherwise conducted similarly. Doubtless the use of large amounts of calcium oxide as suggested by Moissan may serve the purpose of diffusing the explosive mixture through a mass of inert matter sufficient to pre

* Contributions from the Kent Chemical Laboratory of Yale University. From the *American Journal of Science*, vol. vii, 1899.

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vent violent puffing, but care to heat over the radiator as strongly as possible before opening the flame directly to the crucible answers the same end. The difficulty does not exist when acetic acid is used in place of nitric acid, though even in this case it is safer to use the radiator in the first stages of heating, thus avoiding the danger of mechanical loss by too rapid ignition.

Following are determinations made by this method with the use of acetic acid :—

CaO taken. Grm.	B_2O_3 taken. Grm.	B_2O_3 found. Grm.	Error. Grm.
0·9977	0·2065	0·2062	−0·0003
1·0220	0·2067.	0·2070	+0·0003
1·3717	0·2077	0·2075	−0·0002
1·1310	0·1791	0·1795	+0·0004

The results of the preceding table, as well as those of the investigators mentioned, are a sufficient answer to the criticism of Reischle (*Zeitschr. fur Anal. Chem.*, xxvi., 512), that acetic acid and nitric acid do not liberate boric acid in the distillation process so that good results may be obtained. Moreover, it has been shown by one of us (Jones, *Amer. Journ. Sci.*, v., 442) that even carbonic acid is strong enough to bring about complete volatility of boric acid with methyl alcohol.

The Use of Calcium Oxide as a Retainer.

Quite recently Thaddeeff (*Zeitsch. fur Anal. Chem.*, xxxvi., 568) has advocated the abandonment of calcium oxide as an agent for holding boric acid in the evaporation of alcoholic and aqueous solutions, on account of the hygroscopic nature of the oxide and the consequent difficulty of securing it in definite conditions for weighing, and proposes, instead of using calcium oxide, to retain and estimate boric acid in solution by converting it into the form of potassium borofluoride.

In the final modification of Thaddeeff's method the proposal is made to liberate the boric acid from its compounds by sulphuric acid, to volatilise it in methyl alcohol with the aid of a current of dry air, to catch the distillate in potassium hydroxide, to treat the mixture of hydroxide and borate with hydrofluoric acid in excess and evaporate in the steam bath, to digest the residue of fluoride and borofluoride at normal temperatures for two hours with 50 c.m.³ of a potassium acetate solution (sp. gr. 1·14), and for twelve hours more after adding 100 c.m.³ of ethyl alcohol (sp. gr. 0·805), to filter on paper, wash the residue with 62 to 72 c.m.³ of alcohol (sp. gr. 0·805°), dry at 100° and weigh as potassium borofluoride, after which the borofluoride is to be dissolved in boiling water and tested with calcium chloride for possible contamination by the presence of a fluoride. Plainly Thaddeeff's procedure presents at the outset difficulties; for besides the inconvenience of conducting long digestions with reagents of regulated strength, the difficulty of procuring hydrofluoric acid free from silica, which if present (as it usually is, in the so-called chemically pure hydrofluoric acid of commerce) would be retained in the borofluoride as potassium fluosilicate, the inaccuracy of the dried paper filter, and the obvious uncertainty of success in an attempt to wash a mixture of acid potassium fluoride and potassium borofluoride in potassium acetate and alcohol, so that the one shall be rendered entirely soluble while the other remains sensibly unaffected; besides these objections, there is the theoretical probability that boric acid must be lost by volatilisation during the evaporation of the solution of the mixed salts in the presence of free hydrofluoric acid. This last point was put to the proof by submitting to distillation in a platinum retort a mixture of equal quantities of borax and potassium hydroxide with an excess of hydrofluoric acid, collecting the distillate in potassium hydroxide, evaporating it to dryness, and testing it for the presence of boric acid. When this residue from the evaporated distillate was treated with sulphuric acid and methyl alcohol, the burning alcohol vapour gave plainly the green flame of boric acid. Another portion showed clearly the presence of boric acid when acidulated with hydrochloric acid tested with turmeric paper. No boric acid could be detected in any of the reagents used. It is plain, therefore, that boric acid does volatilise upon the evaporation of a mixture of potassium fluoride and borofluoride in acid solution. The amount of such loss is disclosed in the record of the following experiment. Portions of a standard solution of boric acid, prepared by dissolving a known weight of anhydrous boric oxide in a litre of water, were mixed with a solution of potassium hydroxide (free from silica and standardised by conversion to the chloride) in the proportions to form the potassium borofluoride, and an excess of hydrofluoric acid was added. The mixture was evaporated and the residue was dried and weighed at 100°, the whole operation being conducted in platinum.

HKF_2 equivalent to KOH taken. Grm.	B_2O_3 taken. Grm.	$KFBF_2$ theoretical weight Grm.	$KFBF_2$ found. Grm.	Error in terms of $KFBF_2$. Grm.	Error in terms of B_2O_3. Grm.
0·3531	0·1582	0·5701	0·5580	−0·0121	−0·0033
0·3192	0·1430	0·5154	0·5100	−0·0054	−0·0015
0·3192	0·1430	0·5154	0·5030	−0·0124	−0·0034
0·3192	0·1430	0·5154	0·5088	−0·0066	−0·0018
0·3192	0·1430	0·5154	0·5114	−0·0040	−0·0011

In Experiments 1 to 3 the volume of the solution evaperated was about 50 c.m.³. In Experiment 4 this volume was reduced about one-half before acidifying with hydrofluoric acid, while in Experiment 5 the solution was diluted about one-half before adding the hydrofluoric acid. It is plain, therefore, that in this single step of Thaddeeff's process there is a considerable error of deficiency. On the other hand, the errors for the full process as laid down by Thaddeeff have been in our experience invariably differences of excess—presumably because the loss due to volatilisation of boric acid has been overbalanced by the inaccuracy in washing. It is plain that the process can give true indications only by the balancing of considerable errors.

(To be continued).

PROCEEDINGS OF SOCIETIES.

CHEMICAL SOCIETY.

Ordinary Meeting, February 16th, 1899.

Professor Dewar, F.R.S., President, in the Chair.

Mr. W. S. Crouch was formally admitted a Fellow of the Society.

Certificates were read for the first time in favour of Messrs. George Smith Bratby, Oak Field, Hale, Bowdon, Cheshire; John Elias Hughes, Birchville, Wrexham; Lauder William Jones, University of Chicago, Chicago, Ill., U.S.A.; Frederick William Pittuck, 19, Stratford Grove, Newcastle-on-Tyne; Harold McLean Read, 127, Warwick Road, Earl's Court, S.W., Harry Alexander Thiersch, 8, Clifton Gardens, W.; Arthur Luvian Wade, 28, West Kensington Gardens, W.; Charles Walker, Scott Chambers, Pitt Street, Sydney, N.S.W.; Fred Sheasby Watson, Springside, Disley, Cheshire.

A ballot for the election of Fellows was held, and the following subsequently declared duly elected :—

Samuel William Allworthy, M.A.; John Frank Blackshaw; Stuart Blofeld, B.A., B.Sc.; Robert Alfred Bolam, M.D.; Bertram H. Bowles; William H. Branscombe, B.A.; H. Cort H. Carpenter, B.A., Ph.D.; Thomas John Cheater; Frank Cope; Thomas James Cozens; James Washington Epps; Harry Estcourt Estcourt; Ernest

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Barratt Fairweather; George Cecil Fry, B.Sc.; Colin Charlwood Frye; Edmund Vivian Gabriel, M.A.; John Golding; Samuel Godfrey Hall; Henry Winston Harper, M.D.; Harold Brewer Hartley, B.A.; George Ward Hedley, M.A.; James Hembrough; Thomas Anderson Henry; Harold Octavius Knight; Edward Flatman Linstead; Alfred Lucas; Thomas Luxton, B.A., B.Sc.; Thomas Mackenzie; Samuel Montagu Martin; Joshua Maudsley, B.A.; James McCracken; Arthur Mirrlees, B.A.; Bernhard Mohr, Ph.D.; John Cavendish Molson; John Trengrove Nance, B.A.; William Walter Scott Nicholls; Dudley Northall-Laurie; John O'Sullivan; James Henry Pizey; Robert Coleman Price; Horace Seymour Pyne; James Roberts, Jun.; Frederick William Skirrow, B.Sc.; Frederick Soddy, B.A.; Arnold Stevenson, B.A.; Charles Emerique Szarvasy, Ph.D.; Louis Heathcote Walter, B.A.; Arthur Lee White, B.Sc.; Henry Fox White; William Arthur Williams; Thomas Wilson Wormell, B.Sc.

The President announced that Mr. C. E. Groves, F.R.S., had resigned the Editorship of the Society's *Journal*, and that Dr. W. P. Wynne, F.R.S., had been appointed to succeed him. The Council had recorded their sense of Mr. Groves's services to the Society in a vote of thanks, a copy of which would be engrossed on vellum and presented to him at the Anniversary Meeting.

It was announced that the following changes in the Officers and Council were proposed by the Council:—

As *President*—Professor T. E. Thorpe, Ph.D., D.Sc., LL.D., F.R.S., *vice* Professor James Dewar, M.A., LL.D., F.R.S.

As *Vice-Presidents*—Mr. C. E. Groves, F.R.S., and Professor Thomas Purdie, Ph.D., F.R.S., *vice* Professor F. R. Japp, M.A., LL.D., F.R.S., and Professor W. A. Tilden, D.Sc., F.R.S.

As *Hon. Secretary*—Dr. Alexander Scott, F.R.S., *vice* Dr. W. P. Wynne, F.R.S.

As *Hon. Treasurer*—Professor W. A. Tilden, D.Sc., F.R.S., *vice* Professor T. E. Thorpe, LL.D., F.R.S.

As *Ordinary Members of Council*—Mr. H. Brereton Baker, M.A., Professor F. Clowes, D.Sc., Dr. G. T. Moody, and Professor James Walker, D.Sc., *vice* Professor Bedson, D.Sc. Mr. Hehner, Professor McLeod, F.R.S., and Dr. Scott, F.R.S.

Dr. H. T. Brown, F.R.S., Dr. A. W. Crossley, and Mr. R. J. Friswell were appointed to audit the Society's accounts.

Of the following papers those marked * were read:—

*26. "*On the Absorption Spectrum and Constitution attributed to Cyanuric Acid.*" By W. N. Hartley, F.R.S.

The spectrum of cyanuric acid was described by the author in 1882 (*Trans.*, xli., 84), as exhibiting an absorption band between wave-lengths 2747 and 2572, and the formula deduced was that of a symmetrical trihydroxybenzene in which the three CH-groups are replaced by three nitrogen atoms. The bulk of the original preparation having been carefully preserved, its absorption spectrum has been photographed again with the improvements and modifications devised by the author in 1883 (*Phil. Trans.*, 1885, clxxvi., 471). The results show that 2·5 grms. of cyanuric acid, when dissolved in hot distilled water, made up to 500 c.c. and placed in cells respectively 200 m.m. and 100 m.m. in length, exhibited nothing which could be described as an absorption band. In the first case the warm solution cut off the spectrum sharply at about wave-length 2572, but transmitted the rays only weakly from about 3330, and in the 100 m.m. cell the spectrum was cut off sharply at 2483. The spectra thus obtained are in complete harmony with the formula $(H{\cdot}N{:}C{:}O)_3$, but not with that formerly given.

A searching examination of all the conditions and circumstances surrounding the preparation of the solutions and photographs of the original spectra shows that the possibility of any foreign substance getting into the cyanuric acid was almost precluded. But as the specimen was purchased there might have been, perhaps, a m.grm. or less of some solid substance adhering accidentally to the lip of the bottle, or attached to the cork, which would be weighed out with the first quantity of crystals. There are many well-known substances, of which a m.grm. would suffice to produce the effect observed.

*27. "*A Study of the Absorption Spectra of Isatin, Carbostyril, and their Alkyl Derivatives in relation to Tautomerism.*" By W. N. Hartley, F.R.S., and James J. Dobbie, D.Sc., M.A.

In this paper the authors trace the relation between the curves of molecular absorption and the constitution of isatin, carbostyril, and their alkyl derivatives. They start from the fact (*Phil. Trans.*, 1879, clxx., Part I., 257) that the substitution of a methyl or ethyl group for an atom of hydrogen, without other alteration in the structure of the substance, merely increases the general absorption,—*i. e.*, slightly shortens the transmitted spectrum without making any difference in the character of the absorption, and show that when the curves of molecular absorption of the substances studied are compared, a very close resemblance is seen to exist between the parent substance and one of the two isomeric derivatives.

In the carbostyril group the spectra of carbostyril, methylcarbostyril, and methyl- and ethyl-pseudocarbostyril are compared. Carbostyril and methylpseudocarbostyril both show an absorption band in the same position, and the spectra of the two substances are, in other respects, almost identical, the only difference being that the general absorption is slightly increased in the case of methyl- and ethyl-pseudocarbostyril, which is the effect usually produced when alkyl radicles are substituted for hydrogen. The spectra of methylcarbostyril differ in a marked manner from those of carbostyril and methylpseudocarbostyril; the absorption band occupies a different position, is less persistent and less intense than the corresponding band of the latter, and the amount of the general absorption is less.

Isatin and its derivatives show similar relations. In the spectra of isatin there are two absorption bands. The spectra of methylpseudoisatin closely resemble those of isatin, likewise exhibiting two absorption bands, and about the same extent of general absorption. In methylisatin there is only one strong absorption band.

The authors conclude that the very close resemblance between the curves of molecular absorption of carbostyril and methyl- and ethylpseudocarbostyril and between those of isatin and methylpseudoisatin point to identity of constitution, and, inasmuch as the chemical behaviour of methylpseudocarbostyril and methylpseudoisatin show that these compounds are lactams, the lactam constitution must also be assigned to carbostyril and isatin. This conclusion agrees with that arrived at by Goldschmidt and Meissler (*Ber.*, 1890, xxiii., 253), who employed a purely chemical method in their investigations, and with the more recent results of Knorr (*Annalen*, 1896, ccxciii., 81).

A detailed account of the various spectra is given in the paper.

Discussion.

Dr. J. H. Gladstone said that the study of the selective absorption of the rays of light by different substances was a physical method of research which, in his opinion, had been too much neglected. It was capable, beyond doubt, of distinguishing between different compounds of an elementary substance, and, in some instances, of throwing light on their constitution. If the absorption of rays of light by a compound were always the sum of the absorption of its separate constituents, or if different compounds of the same element gave totally different spectra, this mode of analysis would be of little use: investigation showed, however, that similarity is often associated with suggestive differences. Thus, in the case of ferric

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salts, the extreme red ray is always transmitted with the greatest ease, whilst the blue-green and other more refrangible rays are soon absorbed; yet the rapidity of absorption varies very much, as may be seen in the great difference in the degree of redness of such ferric salts as the nitrate and sulphocyanide. Observations such as these were much facilitated by placing the liquid in a hollow prism instead of in a cell with parallel sides, as, in this way, the gradual absorption of the various rays by different thicknesses could be seen and mapped at once. The absorption of different kinds of rays might be employed for the purpose of chemical research, each having, no doubt, its own story to tell, and fruitful results might be expected from the use, not only of the coloured rays of the visible spectrum and of the more refrangible rays which Professor Hartley is engaged in photographing, but also of the less refrangible heat rays, and even, perhaps, of the X rays in the future.

Professor Dobbie pointed out that the relation of such substances as isatin and its methyl derivatives to one another had long been a vexed question, and that it had not been found possible to solve it by means of chemical methods. The advantage of the spectroscopic method was that the uncertainty, due to possible shifting of the atoms in the course of a chemical reaction, did not arise. It was interesting to note that the results obtained by this method were in complete agreement with those most recently arrived at by chemical processes, in which care had been taken to eliminate, as far as possible, the sources of error inseparable from the older methods.

Dr. A. Harden referred to Schiff's work on the isolation of tautomeric forms of ethylic acetoacetate, and asked whether experiments had been made with the object of isolating and of examining spectroscopically the enolic form of isatin.

The President said that every physical method which in any way could aid in establishing the identity of a material under investigation was of the utmost importance to future workers. A substance might seem to be pure so far as evidence derived from ordinary analytical methods was concerned, and yet reveal the presence of impurity when its ultra-violet spectrum was examined. This was the case with water, the ultra-violet spectrum of which was most characteristic, and served to indicate the presence of water vapour in gases dried by the ordinary methods. He was inclined to think that some improvement might be made in the selection of the material for obtaining the ultra-violet spectrum. The cadmium spectrum was open to the objection that wide gaps existed in which no lines were present, and the use of a material such as iron, which gave a spectrum of lines more evenly distributed in the ultra-violet, would seem to be preferable.

Professor Hartley, in reply, said that, when working with rays of high refrangibility, it had been found best to use a quartz cell in which the faces were parallel.

The use of the iron spectrum for the study of absorption spectra had attracted his attention in the past, and was referred to in the paper published in 1879; the objections to its use were that too many lines were present, and that two very strong groups existed in the more refrangible part where absorption bands were likely to occur. The best electrodes for use were those made of cadmium-tin and cadmium-lead alloys containing 15 to 20 per cent of cadmium; the lines were sufficiently numerous and distinct, but not too strong, and there was, moreover, the continuous spectrum between them forming, as it were, a background.

The investigation of tautomeric compounds was in progress, and the results would form the subject of a separate communication to the Society.

**28. "*The Estimation of Nitrites and Nitrates by means of Ferrous Chloride.*" By A. Wynter Blyth.

The author has devised an apparatus in which nitrites and nitrates, either singly or together, can be estimated as nitric oxide by means of ferrous chloride. The essential feature of the apparatus is a mercury valve, which is made by connecting one end of a long delivery tube with the side tube of a flask, and causing the other to dip below the surface of mercury in the mercurial trough, the bend of the delivery tube being 770 m.m. above this level. The air from the flask is expelled by boiling, and a special feature is made of the ease with which successive vacua can be obtained in such a flask. The author has found that nitric oxide is evolved from nitrites at once, whereas there is an appreciable interval of from one to two minutes before any nitric oxide is formed from nitrates. Nitrates yield the whole of the nitric oxide only when the flask is evacuated several times. The results obtained with the apparatus are accurate.

Discussion.

Mr. J. H. Coste said that eight years ago he had used in the laboratory of the Royal Agricultural Society of England an apparatus similar in principle to that described by the author, but of simpler construction. It was, he believed, devised by Dr. Walter Leather, and was described in Addyman's "Agricultural Analysis." The indiarubber stopper of the evolution flask was provided with a water jacket, and fitted with a delivery tube considerably over 760 m.m. in length, dipping under the surface of mercury in a tray placed at a lower level. The use of the rising tube described by the author was thus obviated. The results obtained and the ease in manipulation left little to be desired.

Mr. Wynter Blyth, in reply, stated that he did not claim anything new in the principle of the apparatus; it had, indeed, been applied for some time in the construction of mercury pumps. He was glad to hear that the same kind of valve was in use successfully elsewhere.

*29. "*Estimation of Boric Acid Mainly by Physical Processes.*" By A. Wynter Blyth.

When a methylic alcohol solution of boric acid is distilled, 78 per cent of the acid collects in the first fifth of the distillate; a dilute aqueous solution, on the contrary, loses very little of the acid until concentration has taken place. These facts are applied to the detection of minute traces of boric acid in various substances.

It is shown that even small quantities of boric acid can be estimated by polarimetric methods. For this purpose, 3 grms. of dextrotartaric acid are dissolved in methylic alcohol, and the solution of boric acid in methylic alcohol added so as to make exactly 20 c.c. at 18°. The increase of rotation is then observed. For quantities amounting to 0·05—1·03 per cent, a 5 dm. tube is required The specific rotation, calculated on the constant amount of the tartaric acid present, is given for quantities ranging from 0·05—3 per cent.

When boric acid is boiled with a solution of sodium carbonate carbon dioxide is evolved, in accordance with the equation $Na_2CO_3+4H_3BO_3=Na_2B_4O_7+CO_2+6H_2O$, the proportion being 0·177 part by weight for every part of boric acid present. After boiling and concentrating, the solution is made up to a definite volume, and the conductivity at 18° measured by Kohlrausch's method. From the reduction of the resistance, the amount of boric acid, as sodium borate, can be estimated provided the sodium carbonate solution employed is always of the same strength. A table is given of the values of K (resistance of cell divided by resistance in ohms, of solution), and the results are plotted out as a curve. After the resistance has been determined, an aliquot part or the whole of the solution is transferred to a flask connected with the apparatus described in the preceding abstract, and the carbon dioxide estimated by treatment with an acid.

Discussion.

Mr. A. C. Chapman pointed out that small quantities of impurities in the boric acid would be likely to sensibly affect the accuracy of physical methods such as those suggested by the author, and asked how the whole of the boric acid could be obtained from such substances as

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food products in a state of sufficient purity for the application of these methods.

Mr. WYNTER BLYTH, in reply, said that distillation with methylic alcohol gave the methyl compound in a state of sufficient purity for the purpose of estimation by the polarimetric method.

30. "*The Interaction of Ethylic Sodiomalonate and Mesityl Oxide. A Correction.*" By ARTHUR W. CROSSLEY.

Since the publication of a preliminary notice on the action of ethylic sodiomalonate on mesityl oxide (*Proc.*, 1898, xiv., 247) Dr. Vorländer of Halle has pointed out to the author that the reaction has already been studied. The substance obtained by hydrolysis of the condensation product is dimethylhydroresorcine, $C_8H_{12}O_2$, and possesses half the molecular weight assigned to it by the author, and although having marked acid properties is not a carboxylic acid.

The author expresses his regret at not having known of Dr. Vorländer's work.

31. "*On Lössner's Benzoylethyloxysulphocarbamic Acid, and the Formation of Pseudoureas.*" By AUGUSTUS EDWARD DIXON, M.D.

Benzoyl chloride interacts with a hot saturated solution of potassium thiocyanate, yielding potassium chloride and a compound, $C_{10}H_{11}NSO_2$, regarded by Lössner (*Journ. Prakt. Chem.*, 1874, [ii.], x., 237) as benzoylethyloxysulphocarbamic acid, COPh·NEt·CO·SH. Miquel (*Ann. Chim. Phys.*, 1877, [v.], xi., 334), showed later that the same compound is produced from benzoylthiocarbimide and ethylic alcohol, and that consequently it is not an acid, but an "ether," COPh·NH·CS·OEt. With caustic potash, it affords a potassium derivative, from which by interaction with ethylic iodide, the corresponding ethylic compound is obtained; the latter is decomposed by ammonia into mercaptan, together with a supposed unsymmetrical benzoylethylurea, COPh·NEt·CO·NH$_2$.

In the present paper, it is shown that the constitution assigned to this "urea" is not in accordance with its properties. On hydrolysis, it yields carbonic and benzoic acids, alcohol, and ammonia, but no ethylamine, from which it follows that the ethylic group is not attached to nitrogen, and the conclusion is drawn that the supposed urea of Lössner is really the ethylic salt of a benzoylated imidocarbamic acid, COPh·N:C(OEt)·NH$_2$. Corresponding compounds have now been obtained, which bear towards the ureas a relation similar to that subsisting between the pseudothioureas and the thiocarbamides: to maintain uniformity of nomenclature, it is proposed that such imido-derivatives of organic salts of carbamic acid should be termed pseudoureas generically.

The constitution attributed by Lössner to the ethylic derivative from which the above ethyl-ψ-*n*-benzoylurea is obtained is COPh·NEt·CO·SEt; its properties, however, are inconsistent with this structure, and the author assigns reasons for representing it by the formula COPh·N:C(OEt)·SEt. If the potassium compound from which the latter is produced be similarly constituted, Miquel's formula for Lössner's benzoylethyloxysulphocarbamic acid requires further modification into that of the tautomeric ethylic imidobenzoylthiocarbonate, COPh·N:C(OEt)·SH.

Methyl-ψ-n-benzoylurea, COPh·N:C(OMe)·NH$_2$, is deposited from light petroleum in fern-like masses of white, flattened crystals, melting, without decomposition, at 77—78°. When boiled with alkali, or heated with water at 150—160° under pressure, it is hydrolysed into carbonic and benzoic acids, ammonia, and methylic alcohol; no ethylamine could be detected. Its isomeride, *ab-benzoylmethylurea*, COPh·NH·CO·NHMe, is prepared by desulphurising the corresponding thiocarbamide with silver nitrate; the thiocarbamide separates from alcohol in tufts of shining needles, the urea in colourless, thick prisms; they melt at 152° and 171° respectively.

Ethyl-ψ-n-benzoylurea, COPh·N:C(OEt)·NH$_2$, forms rhombohedral crystals melting at 74—75° without decomposition. Its isomeride, *ab*-benzoylethylurea, is stated by Miquel to melt at 192°, or, according to Leuckhart (*Journ. Prakt. Chem.*, 1880, [ii.], xxi., 33), at 168°. When prepared from the thiocarbimide (m. p. 130—131°) by means either of silver nitrate or, as described by Miquel, of yellow oxide of mercury, it was found to melt at 114—115°.

Anisoilthiocarbimide, OMe·C$_6$H$_4$·CO·NCS, is obtained, in solution, by heating the corresponding chloride, OMe·C$_6$H$_4$·COCl, dissolved in benzene, with lead thiocyanate. It unites with alcohol, forming *anisoilthiourethane* or, *ethylic imidoanisoilthiocarbonate*,

OMe·C$_6$H$_4$·CO·N:C(SH)·OEt,

which crystallises in small, white needles melting at 70—71°. The *potassium derivative* of the latter melts at about 222° (uncorr.); when boiled in alcoholic solution with ethylic iodide, and then saturated with ammonia, it yields *ethyl-ψ-n-anisoilurea*, OMe·C$_6$H$_4$·CO·N:C(OEt)·NH$_2$, in white, transparent prisms melting at 69—70°.

Anisoilthiocarbimide unites spontaneously with nitrogenous bases forming thioureas and thiocarbamides; the following are described. *Anisoilthiourea*, CSN$_2$H$_3$·C$_8$H$_7$O$_2$, forms rhombs and octahedra melting at 216—217°. By fusion with chloracetic acid, it yields *anisoilthiohydantoin* [*n*-anisoilthiourantoin (*Trans.*, 1897, lxxi., 638)], a pale-yellow solid, nearly insoluble in the ordinary solvents, and decomposing between 222° and 230°. *ab-Anisoilphenylthiocarbamide* crystallises from alcohol in brilliant prisms melting at 126°; the corresponding *ortho-* and *para-tolyl* compounds melt at 126·5° and 127—128° respectively. *ab-Anisoilmethylthiocarbamide* melts at 143—144°; the *ethylic* homologue melts at 126·5—127·5°, and yields, on desulphurisation, the symmetrical urea, C$_8$H$_7$O$_2$·NH·CO·NHEt, isomeric with the above ψ-compound; it melts at 146—147°. *ab-Anisoilbenzylthiocarbamide* forms colourless prisms melting at 127—128°. *n Anisoil-ν-phenylbenzylthiourea*, C$_8$H$_7$O$_2$·N:C(SH)·NPhBz, from the thiocarbimide and benzylaniline, occurs in brillant rhombic plates melting at 142—143°. It not desulphurised by boiling with alkaline solution of lead, in which respect it differs from the other anisoil thio-compounds described.

32. "*On Certain Isomeric Tertiary Benzylthioureas.*" By AUGUSTUS EDWARD DIXON, M.D.

n-Phenyl-ν-methylbenzylthiourea,—

NPh:C(SH)·NMe·CH$_2$Ph,

was obtained, in quantitative amount, from phenylthiocarbimide and methylbenzylamine; it formed long, brilliant, silvery prisms melting at 129—130°. Its isomerides, NMe:C(SH)·NPhBz, and NBz:C(SH)·NMePh, melt at 121° and 85° respectively. By desulphurisation with silver nitrate, it afforded the *urea*, NHPh·CO·NMeBz, which crystallised in thin, pearly needles, melting at 134—135°.

n-Benzyl-ν-methylbenzylthiourea, NBz:C(SH)·NMeBz, prepared from benzylthiocarbimide and methylbenzylamine occurred in vitreous needles melting at 73°. Its isomeride, *n-methyl-ν-dibenzylthiourea*, NMe:C(SH)·NBz$_2$, formed white, rhombic crystals melting at 110—111°.

n-Methyl-ν-methylbenzylthiourea, NMe:C(SH)·NMeBz, formed vitreous, flattened crystals melting at 87·5—88·5°. Its isomeride, *n-benzyl-ν-dimethylthiourea*, NBz:C(SH)·NMe$_2$, crystallised in vitreous prisms melting at 98·5—99·5°.

These thioureas are practically insoluble in water; they are unaffected by boiling with alkaline lead tartrate, but are readily desulphurised by warming with nitrate of silver. It was remarked in 1893 (*Trans.*, lxiii., 540) that amongst the then known phenylated isomeric tertiary thioureas, the member containing the NPh-group had the highest melting-point; it is now shown that, in the methylphenylbenzyl series, this is also the case.

33. "*Is Camphene Unsaturated.*" By J. E. MARSH.

The more recent formulæ for camphor, such as that of Bredt, represent camphene, the typical hydrocarbon of

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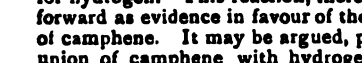
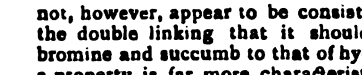
the group, as an unsaturated compound with one double linking. The reactions which appear to support this view are, firstly, the conversion of camphene into camphene glycol, $C_{10}H_{16}(OH)_2$, by the action of potassium permanganate (Wagner, *Ber.*, 1890, xxiii., 2307), and, secondly, the production of camphene dibromide, $C_{10}H_{16}Br_2$, by the action of bromine on camphene (Reychler, *Ber.*, 1896, xxix., 900). These reactions would be sufficient to establish the unsaturated character of camphene if it were a matter quite free from doubt that camphene glycol and camphene dibromide are the simple additive compounds they appear at first sight to be. The so-called camphene glycol, however, appears to possess none of the properties of a true glycol; and, in particular, the fact that it readily loses water, forming a compound having all the properties of an aldehyde, seems to be inconsistent with the view that it is a glycol at all. Moreover, the action of permanganateon camphene is much slower than is usually the case with an unsaturated compound. With regard to camphene dibromide, experiments have been made by the author which lead him to believe that this compound is not formed by the direct union of bromine and camphene, but is really the product of the interaction of bromine and camphene hydrobromide. By saturating camphene dissolved in glacial acetic acid with hydrogen bromide, and then adding bromine to the product, the so-called camphene dibromide is obtained in amount equal to about 70 per cent of the theoretical yield, whereas Reychler, by the direct action of bromine on camphene, obtained only 8 grms. from 27·7 grms. of camphene, which represents a yield of about 13 per cent. The chief product of the action of bromine on camphor is the substituted derivative bromocamphene, $C_{10}H_{15}Br$. In this reaction, then, it appears that bromine first replaces hydrogen in camphene, forming bromocamphene and hydrogen bromide; the hydrogen bromide is partly given off in the gaseous form, but in part also combines with the excess of camphene, forming camphene hydrobromide, which is then further acted on by bromine, giving the so-called camphene dibromide by the substitution of bromine for hydrogen. This reaction, therefore, cannot be brought forward as evidence in favour of the unsaturated character of camphene. It may be argued, perhaps, that the direct union of camphene with hydrogen bromide is in itself sufficient evidence of its unsaturated character. It does not, however, appear to be consistent with the nature of the double linking that it should resist the action of bromine and succumb to that of hydrogen bromide. Such a property is far more characteristic of the trimethylene ring, as Professor Perkin has shown, and may be characteristic also of other ring formations.

34. "*Formation of α-Pyrone Compounds and their Transformation into Pyridine Derivatives.*" By Siegfried Ruhemann.

The substances formed from α-pyrone derivatives by the addition of two molecular proportions of ammonia (*Proc.*, 1899, xv., 6), have been transformed into pyridine compounds. The view already expressed, that these additive products may be regarded as ammonium salts of unsaturated amino-acids, readily explains such a change. The transformation is effected by preparing from the ammonium salts the corresponding ethylic salts, which, on distillation, lose alcohol and condense to the pyridine compounds represented by the formulæ:—



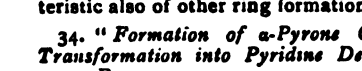
I. M.-p. 184°.



II. M.-p. 210°.

From the ethylic salt represented by formula I., the corresponding acid was prepared; this loses carbon dioxide at 240°, forming phenylmethylpyridone (m. p. 207—208°).

β-Diketones, like ethylic salts of β-ketonic acids, condense with ethylic phenylpropiolate under the influence of sodium ethoxide, forming α-pyrone derivatives of the general formula—



in which R and R' denote hydrocarbon radicles. Thus, from acetyl-acetone and from benzoylacetone, compounds have been obtained which melt respectively at 128° and 143—144°, and behave like α-pyrone derivatives with alcoholic ammonia.

Anniversary Meeting.

The Anniversary Meeting will be held on Wednesday, March 29th, at 3 o'clock in the afternoon.

CORRESPONDENCE.

THE ESTIMATION OF MANGANESE BY MEANS OF POTASSIUM PERMANGANATE.

To the Editor of the Chemical News.

Sir,—In my letter of February 3rd (Chemical News, vol. lxxix., p. 58), I intended to intimate that the low results obtained when estimating manganese by an iron standardised solution of potassium permanganate were not due to carbon either in the case of the method described by Mr. Brearley (Chemical News, vol. lxxv., p. 15), or in that recently described by myself (Chemical News, vol. lxxix., p. 25), and that the oxides precipitated in Mr. Brearley's method are therefore also "deficient in oxygen." This, of course, is immaterial when the solution is standardised in the same manner as the subsequent titrations are performed.

In regard to the method to which Mr. Brearley considers Gooch and Austen have applied the "faint praise which damns," I wish to remark that the method is their own, *not mine*, and that when I drew attention to their work to show that the presence of burnt gases had not that fatal effect Mr. Brearley would like to show they have I did not intend to endorse their method of applying them.

I am quite aware of the work done by Pickering—in fact, it would be difficult to miss these oft quoted figures; but I cannot say I have found the oxide variable when working under the conditions I describe. As an instance out of many, I give four estimations of manganese made recently on the same ferro by two operators working with platinum crucibles of varying size and thickness. The figures obtained were:—

1	.. ..	80·78 per cent Mn
2	.. ..	80·78 ,,
3	.. ..	80·72 ,,
4	.. ..	80·74 ,,

This cannot be said of ignition in a muffle unless it is very hot, and with the muffles in this laboratory it often happens they are not hot enough to make an accurate ignition of Mn_3O_4. This must happen in many instances where muffle furnaces are coke fired.

The following estimations of manganese in the same ferro will show the effect of temperature:—

5. The precipitate was heated in a muffle at bright red heat (say about 850° C.) for fifteen minutes, giving—

Mn .. .. 82·22 per cent.

The same precipitate was then heated over the blowpipe for three minutes, with the result that the figure obtained was the same as in the above four estimations, viz.—

Mn .. .. 80·78 per cent.

6. Another precipitate was heated in a muffle at red heat for two hours, which gave a result—

Mn .. .. 84·02 per cent,

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The precipitate was then heated over the blowpipe for five minutes, giving—

Mn .. .. 80·74 per cent.

Two estimations were then made in a muffle at white heat (silver melted easily).

7. The precipitate was heated in a white-hot muffle for thirty minutes.—

Mn .. .. 80·88 per cent.

It was then heated over the blowpipe, the weight remaining constant—

Mn .. .. 80·88 per cent.

8. Another precipitate was heated in a muffle at white heat for thirty minutes, and gave—

Mn .. .. 80·78 per cent.

When heated over the blowpipe the result was the same—

Mn .. .. 80·78 per cent.

An estimation was then made by heating a precipitate over the blowpipe for a very much longer time than usual.

9. The precipitate was heated over blowpipe for five minutes—

Mn .. .. 81·02 per cent.

It was then heated fifteen minutes—

Mn .. .. 81·00 per cent.

And again fifteen minutes.—

Mn .. .. 81·00 per cent.

This estimation does not agree so well as the others, but it, however, shows that the continued action of the gases have no marked effect on the weight of the precipitate.

The impurities in all the above cases were removed as described in my recent article (CHEMICAL NEWS, lxxix., p. 25).

In the estimation of manganese as Mn_3O_4, it seems to me that the variability of the oxide is allowed to play too much the part of a "red herring," withdrawing attention from the very important fact that almost invariably impurities are present in the precipitate and must be removed. If these are ignored when working on 0·5 grm. of an 80 per cent ferro I have found an error of quite 1 per cent is sometimes introduced; silica is always present, derived presumably partly from the flask, and partly from the ferro; a black precipitate of iron, &c., with H_2S is also almost always present, and in the case of ores containing *lime* as much as 1·5 per cent will often be precipitated with the manganese. As an instance of how this error is usually ignored I may point out that Arnold ("Steel Works Analysis," p. 206), gives all due prominence to the possibility of the oxide varying, but mentions nothing about the probability of impurities being present.

In the method there described, however, precautions are certainly taken to prevent the presence of iron.

In conclusion, I am glad that Mr. Brearley allows that it is not impossible to obtain Mn_3O_4 in the manner I have described, and I presume I may infer that he will allow that if it is not impossible to do so once, it is not impossible to do so any number of times under the same conditions.—I am, &c.,

F. W. DAW.

Ebbw Vale, February 28, 1899.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

NOTE.—All degrees of temperature are Centigrade unless otherwise expressed.

Comptes Rendus Hebdomadaires des Séances, de l'Académie des Sciences. Vol. cxxviii., No. 3, January 16, 1899.

Peroxidation of Cerium Dissolved in Alkaline Carbonates.—André Job.—Cerium dissolved in alkaline carbonates can exist in three states. (1) Cerous state, which corresponds to the oxide Ce_2O_3; (2) Ceric state, CeO_2; and (3) Perceric state, CeO_3. The author proves that the capacity of oxidation by air depends, in a great measure, on the nature of the salt which is dissolved in the alkaline carbonate. Thus, a solution of ammoniacal ceric nitrate remains in the ceric state in the air, without even the commencement of peroxidation, whilst a cerous solution of the nitrate passes at once into the ceric state, and then continues to fix the oxygen of the air, until a limit is reached which depends on the dilution.

The Source of Energy in Radio-active Bodies.—Sir William Crookes.—The author, referring to M. and Mdme. Curie's recent discovery of the new radio-active substances polonium and radium, states that the radiant activity of the new bodies needs neither the excitation of light nor the stimulus of electricity, but like uranium it draws its energy from some constantly regenerating and hitherto unsuspected store, exhaustless in amount. It can be conceived that uranium, polonium, and radium—bodies of densest atoms—have a structure that enables them to throw off the slow moving molecules of the atmosphere, while the quick moving molecules, smashing on to the surface, have their energy reduced, whilst the energy of the body is correspondingly increased. The energy thus gained seems to be employed partly in dissociating some of the molecules of the gas, and partly in originating an undulation through the ether, which, as it takes its rise in phenomena so disconnected as the impacts of the molecules of the air, must furnish a large contingent of light waves of short wave-length. The shortness in the case of these Becquerel rays appears to approach, without attaining the extreme shortness of ordinary Röntgen rays. The reduction of the speed of the quick moving molecules would cool the layer of air to which they belong, but this cooling would rapidly be compensated by radiation and conduction from the surrounding atmosphere; under ordinary circumstances, the difference of temperature would scarcely be perceptible, and the body would thus appear to perpetually emit rays of energy with no apparent means of restoration.

Triacetyl-morphine and Oxidation of Morphine.—H. Causse.—By the action of acid chlorides or anhydrides on morphine, $C_{17}H_{19}NO_3$, it has been shown that two of the oxygen atoms are in hydroxyl-groups—one phenolic, the other alcoholic. Attempts to prepare tri-substituted derivatives have so far been unsuccessful, and the author now demonstrates that the third oxygen atom of morphine is contained as carbonyl, CO, and that it is possible to obtain a triacetyl-derivative. The latter is a colourless crystalline body, insoluble in water, and giving no coloration with ferric chloride. Analysis ascribed to it the formula $C_{17}H_{17}N(C_2H_3O_2)_3.H_2O$. To confirm the presence of a CO group in morphine, oxidation was applied by means of iodic acid, the resulting CO_2 passed into baryta-water, and the barium carbonate separated and titrated. The CO_2 thus estimated corresponded to $C_{17}H_{19}NO_3 - CO_2$, or one molecule of carbonic acid for one molecule of morphine. Hence morphine may be written—

$$C_{16}H_{17}N\begin{matrix}OH\\OH.\\CO\end{matrix}$$

No. 4, January 23, 1899.

Properties of Aluminium.—A. Ditte.—In a former paper the author has shown that aluminium, though apparently unaltered by many chemical reagents, is in reality easily acted upon; this property not being apparent owing to a thin layer of alumina or gas being formed over the surface of the metal. He now continues his researches by examining whether the reactions are the same in the presence or absence of air, and shows that the alteration of the aluminium is distinctly facilitated by using atmospheres of oxygen and carbonic acid. The experiments are conducted with a mixture of sea-salt and acetic acid.

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Researches on the Chemical State of some Elements contained in Siderurgical Products, Double Carbides of Iron, and other Metals.—Ad. Carnot and M. Goutal.—The authors show the existence of a certain number of well-defined carbides in siderurgical products. The following are the ones which have been isolated:—$3Fe_3C.Cr_3C_2$, $Fe_3C.3Cr_3C_2$, $Fe_3C.W.C$, $Fe_3C.Mo_2C$, $2Fe_3C.Mn_3C$, $Fe_3C.2Mn_3C$, $Fe_3C.4Mn_3C$.

Action of Oxidising Agents on certain Aromatic Compounds.—Œschner de Coninck and A. Combe.—The authors have further investigated the action of the chromic acid mixture on certain nitrogenous derivatives of the aromatic series with the object of discovering if there were no disengagement of nitrogen at the end of the reaction. In all cases they obtained only pure carbon dioxide—thus confirming their previous conclusions.

Action of Iodine Chloride on Monochlorbenzene in presence of Anhydrous Aluminium Chloride.—M. Friedel.—The author has investigated a new method of preparing chloriodine derivatives of the aromatic series. The method generally in use is that of digesting chloramines, and replacing the NH_2 groups by an atom of iodine. In the method here discussed, the chloro-derivatives themselves form the starting-point, and iodine is directly substituted for a hydrogen atom of the nucleus by means of boiling ClI. The reaction may be expressed as follows:—$C_6H_mCl_n + ClI = C_6H_{m-1}Cl_nI + HCl$, and takes place in presence of anhydrous aluminium chloride. A description of the preparation of para-iodo-chlorbenzene is given.

Biochemical Oxidation of Propylglycol.—André Kling.—Up to the present, no general method has existed of preparing glycols. After the publication of G. Bertrand's work on the oxidising action of the sorbose bacterium on polyvalent alcohols, André Kling applied the method to the case of glycols, and discovered oxidation to occur in a similar manner. The experimental substance was propyl glycol. This was treated with a culture of the sorbose bacterium for twenty days, after which the solution obtained was found to reduce Fehling's solution. The oxidation product was isolated by means of phenylhydrazin hydrochloride, being obtained as a yellow precipitate. The author intends to investigate the possibility of generalisation of this reaction.

Berichte der Deutschen Chemischen Gesellschaft.
Vol. xxxi., April 25, 1898.

The Salts of Pertungstic and Permolybdic Acids.—P. Melikoff and L. Pissarjewsky.—When the hypertungstates and hypermolybdates of K and Na are carefully heated with H_2O_2, mixed compounds of Na_2O_2, K_2O_2, and H_2O_2 are obtained. The authors have thus prepared and analysed the following compounds:—

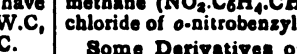
$$Na_2O_2WO_4H_2O_2 + (Na_2O_2)^2WO_4 + 7H_2O,$$
$$Na_2O_2WO_4H_2O_2,\ K_2O_4WO_3H_2O_2, \text{ and } K_2O_2.MoO_3.H_2O_2.$$

The Hypertitanates and Hyperborates.—P. Melikoff and L. Pissarjewsky.—The compound $NaOBO_3$ has not yet been obtained, but by adding an excess of H_2O_2 to a saturated solution of borax containing the equivalent quantity of NaHO, slightly soluble crystals are deposited in the form of monoclinic prisms; they are stable in the air, soluble in water at the ordinary temperature, and, by the action of dilute H_2SO_4, they give H_2O_2; their composition corresponds to the formula $NaBO_3 + 4H_2O$. By the action of H_2O_2 on the alkaline hypertitanates the two following crystalline compounds are obtained:—

$$(K_2O_4)_2TiO_3 + 10H_2O \text{ and } (Na_2O_2)_4Ti_2O_7 + 10H_2O.$$

The Condensation of Nitromethane with the Substituted Aromatic Aldehyds.—Th. Posner.—While the aldehyds of the fatty series react violently with nitromethane, the action of the aromatic aldehyds only takes place in the presence of condensation agents with the elimination of water. By heating 5 grms. of *o*-nitrobenzaldehyd up to 160° for eight or nine hours with 2 grms. of nitromethane and 0·5 grm. of chloride of zinc, the author obtained *o* nitrophenylnitroethylene (*ω-o*-dinitrostyrol); he also prepared di-*o*-nitrobenzylnitromethane $(NO_2.C_6H_4.CH_2)^2 + CH.NO_2$, by the action of chloride of *o*-nitrobenzyl on nitromethane soda.

Some Derivatives of Pyrocatechin.—Julius Hesse.—When di-soda pyrocatechin, suspended in alcohol, is heated for sixteen hours at 200° with dichloracetal, in a sealed tube, an oil is formed insoluble in the alkali, which is 1·2-phenylene-diethylorthoglyoxal,—



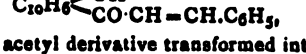
It is a volatile liquid with a density of 1·1252 at 14°, and boils at 150° with a pressure of 22 m.m.; concentrated H_2SO_4 colours it a reddish-violet.

A New Method for the Acetylation of the Amide Derivatives.—B. Pawlewski.—This method consists in making thioacetic acid react on the amide derivatives; the disengagement of SH_2 in this reaction, instead of H_2O as in the ordinary acetylation does not hinder the formation of the derived amide so much. The reaction is generally immediate, the products pure, and the return excellent—$RNH_2 + CH_3.CO.SH = R.NH.CO.CH_3 + H_2S$.

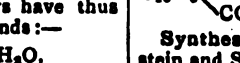
Action of the Primary, Secondary, and Tertiary Bases on Bromide of *o*-Xylylene.—A. Partheil and Th. Schumacher.—By causing bromide of *o*-xylylene to react on aniline the authors obtained dianilide of the *o*-xylylene, and with the *o*-toluidine the corresponding derivative; they also describe the derivatives of *p*-phenitidine and piperidine. They are unable to confirm Scholtz's observations that the tertiary amines cannot react on bromide of *o*-xylylene except with the formation of di-ammonium compounds.

Synthesis of 3 Oxyflavone.—T. Emilewicz and St. v. Kostanecki.—The authors used the ethoxyl derivative of *o*-oxybenzalacetophenone obtained by condensing benzaldehyd with resacetophenone, and then prepared 3-ethoxyflavone, $C_{15}H_9O_2(O_2H_5)$, which, by prolonged boiling with HI of density 1·7, was converted into 3-oxyflavone, $C_{15}H_9O_2(OH)$.

On α-Naphthoflavone.—St. v. Kostanecki.—2-aceto-1-naphthol condensed with benzaldehhyd gives 2-benzal-aceto-1-naphthol,—



of which the acetyl derivative transformed into dibromide gives, by the action of alcoholic potash, α-naphthoflavone,



, fusible at 154—156°.

Synthesis of the Flavone Derivatives.—W. Feuerstein and St. v. Kostanecki.—By the elimination of water from 2-oxybedzaldiacetophenone, the authors obtained a compound enclosing an oxygenated hexagonal nucleus.—

This compound is modified by boiling with mineral acids, and a substance corresponding to the formula $C_{23}H_{16}O_2$ is formed; this compound no longer contains the hydroxyl group.

The Oxybenzalbromindanones.—W. Klobski and St. v. Kostanecki.—The authors have examined the derived hydroxylised colouring-matters of benzalindanone, but as indanone itself was difficult to prepare they used one of its derivatives, 2-bromindanone. Bromindanone reacts very easily with benzaldehyd and gives 2-brom-benzalindonone. The three isomerous monoxybenz-

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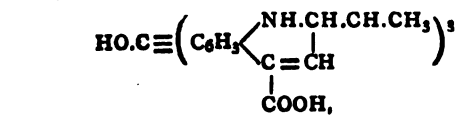
aldehyds also condense with bromindanone in the presence of soda-lye. The authors describe several oxybrombenzalindanones thus obtained, as well as some of their derivatives.

Glauconic Acids, a New Group of Colouring-matters from Quinolein. — O. Doebner. — Under this name the author describes a series of acids of colouring-matters obtained by the double decomposition of aniline and its *p*-alcoyl derivatives with pyruvic acid and formaldehyd. Glauconic acid prepared by means of aniline is comparable to *p*-rosaniline, $HO.C\equiv(C_6H_4NH_2)_3$. It is a product of condensation of the carbinol group HO.C with 3 molecules of dihydro-α-methyl-cinchonic acid,—



or an anhydride of this body.

MISCELLANEOUS.

The Chemical Laboratory at Wiesbaden. — The Chemical Laboratory Fresenius has during the Winter Term of 1898-99 been attended by forty-five students. Of these, thirty were from Germany, three from England, two respectively from Holland, Russia, and Brazil, and one from Austria, France, Norway, the United States of North America, the South African Republic, and India. Among those studying were several who were preparing for the Final Examination of Food Chemistry. There were three Assistants in the Instruction Laboratory, and twenty-four in the Experimental part (Examining Laboratories). No changes have taken place in the teaching staff of the Institution, to which, besides the Directors—namely, Herr Prof. Dr. H. Fresenius, Prof. Dr. W. Fresenius, and Prof. Dr. E. Hintz—belong Herr Dr. med. G. Frank, Dr. W. Lenz, Dr. L. Grünhut, and Architect J. Huber. The Summer Term begins on April 24th next. In this Winter Term, besides scientific work, there were many examinations carried on in the Experimental part (Examining Laboratories) in the interest of trade, industry, mining, farming, health, justice, and government.

MEETINGS FOR THE WEEK.

Monday, 6th.—Society of Arts, 8 (Cantor Lectures). "Cycle Construction and Design," by Archibald Sharpe A.M.Inst.C.E.

— Royal Institution, 5. General Monthly Meeting.

Tuesday, 7th.—Royal Institution, 3. "The Morphology of the Mollusca," by Prof. E. Ray Lankester, M.A., LL.D.

Wednesday, 8th.—Society of Arts, 8. "Cornish Mines and Miners," by J. H. Collins, F.G.S.

Thursday, 9th.—Society of Arts, 4.30. "Leprosy in India," by H. A. Acworth, C.I.E. (This Meeting will be held at the Imperial Institute).

— Royal Institution, 3. "English Playhouses in the Sixteenth, Seventeenth, and Eighteenth Centuries," by Willian Poel.

Friday, 10th.—Physical, 5. "A Study of an Apparatus for the Determination of the Rate of Diffusion of Solids dissolved in Liquids" and "Note on the Source of Energy in Diffusive Convection," by Albert Griffiths, M.Sc. An Exhibition of Dr. A. Wehnelt's Electrolytic Current Interruptor for Ruhmkorff Coils, by A. A. Campbell Swinton.

— Royal Institution, 9. "Measuring Extreme Temperatures," by Prof. H. L. Callendar, M.A., F.R.S.

Saturday, 11th.—Royal Institution, 3. "The Mechanical Properties of Bodies," by The Right Hon. Lord Rayleigh, F.R.S., &c.

Mr. J. G. LORRAIN, M.I.E.E., M.I.M.E, M.S.C.I.,
Fellow of the Chartered Institute of Patent Agents,
Norfolk House, Norfolk Street, London, W.C.
"PATENTEE'S HANDBOOK" Post Free on application.

GUY'S HOSPITAL.

Entrance Scholarships in September, 1899.—Six Open Scholarships, three (£150, £60, and £50) in Science, and three (£100, £50, and £30) in Arts.—Particulars and copies of Examination Papers on application to the Dean, Guy's Hospital, London Bridge, S.E.

GUY'S HOSPITAL.

Preliminary Scientific (M.B., Lond.).—Classes are held throughout the year. Special instruction is given for the July Examination. Fee, 16 guineas.

BOROUGH POLYTECHNIC INSTITUTE.
103, BOROUGH ROAD, S.E.

The Governors of the above Institute invite applications for the post of ASSISTANT in the CHEMISTRY DEPARTMENT. Salary, £120 per annum. Candidates will be required to undertake the Teaching of classes in the Technical Day School and in the Evening Department. Full particulars may be obtained from the Principal.—Applications, accompanied by not more than three recent testimonials, should be sent in before March 6th, addressed to—

C. T. MILLIS, Principal,
Education Department.

THE YORKSHIRE COLLEGE, LEEDS.

DEPARTMENT OF LEATHER INDUSTRIES.

Applications will be received up to March 16th for the Appointment of ASSISTANT LECTURER and DEMONSTRATOR in LEATHER INDUSTRIES. A sound training in Chemistry is essential; Technical Knowledge, although desirable, is not indispensable. Salary to commence at £150 a year.—Further particulars may be obtained from the Secretary of the College.

CHEMICAL LABORATORY,
WIESBADEN, GERMANY.

DIRECTORS.

Practical Instruction in the Laboratory .. .. Prof. H. FRESENIUS, Ph.D.
Prof. W. FRESENIUS, Ph.D.
Prof. E. HINTZ, Ph.D.

LECTURES.

Experimental Chemistry (Inorganic) — Prof. H. FRESENIUS, Ph.D.
Experimental Physics .. .. — Prof. W. FRESENIUS, Ph.D
Stöchiometry .. ..
Organic Chemistry .. .. — L. GRÜNHUT, Ph.D.
Chemical Technology .. ..
Microscopy, with exercises in Microscopic work .. .. — W. LENZ, Ph.D.
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THE CHEMICAL NEWS.

Vol. LXXIX., No. 2050.

DEPOSITION OF BARIUM SULPHATE AS A CEMENTING MATERIAL OF SANDSTONE.*

By FRANK CLOWES, D.Sc.,
Emeritus Professor, University College, Nottingham.

Some years ago I described the occurrence of a peculiar sandstone over a large area in Bramcote and Stapleford, near Nottingham (*Roy. Soc. Proc.*, xlvi., 363). The sandstone was remarkable for its high specific gravity, and chemical analysis, supported by microscopical examination, proved that the high specific gravity was due to the existence in the sandstone of a large proportion of highly crystalline barium sulphate. In the rock itself the percentage of the sulphate varied from 33·3 to 50·1; and it evidently served as the binding or cementing material which held the sand grains together. The occurrence of this sandstone was stated by geologists to be unique in the United Kingdom.

Mr. J. J. H. Teall made an examination of a portion of the sandstone, and stated that, after breaking up a portion of the rock, he easily effected a separation of the sulphate from the sand by shaking the powder about in water: the small cleavage flakes thus obtained gave the optical characters of crystallised barium sulphate. Mr. Teall further stated that the barium sulphate occurred in large irregular crystalline patches, which included the sand grains; the sand grains, therefore, interrupted the reflections from the cleavage surfaces of the barium sulphate, giving rise to the appearance generally known as "lustre mottling" in petrographic literature.

I had noted this irregular distribution of the barium sulphate. In some parts of the rock the sulphate occurred in reticutated veins inclosing small patches of more or less loose sand grains; while in other parts of the rock the sulphate occurred in spherical or oval masses, between which looser sand was interspersed: occasionally, however, the barium sulphate was uniformly distributed.

The appearance presented by the weathered surface of the rock varied much according to the mode in which the resistant sulphate was distributed. When it was uniformly diistributed it formed an almost complete protection against weathering: this was seen on the cap of the great pillar of this rock, which is locally known as the "Hemlock Stone." The reticulated distribution of the sulphate caused the surface of the weathered rock to present a fretted surface, with the thin veins of sulphate projecting from the surface. When the sulphate had bound together spherical or oval masses in the substance of the sand, these were left in pebble-like forms as soon as the loose sand had been washed out from between them; and the resulting layers of loose sand, inclosing the rounded masses of sand bound together by the sulphate, had been not unnaturally classed by the geologists who had visited the district, as pebble-beds.

In discussing various ways in which this barium sulphate might have been deposited, I drew attention to the frequent deposition of barium sulphate from colliery water in the neighbourhood of Newcastle-upon-Tyne, and described some of these deposits (*Roy. Soc. Proc.*, June, 1889). And I further pointed out that Dr. Bedson had shown (*Journ. Soc. Chem. Ind.*, vi., 712) that barium chloride was a common constituent of the colliery waters in the district in which these barium sulphate deposits occur, and that it was present to the extent of 137·2 parts per 100,000 in some of these waters. It was evidently only necessary that water containing sulphuric acid or a soluble sulphate should mingle with the barium chloride water in order to explain the deposition of barium sulphate in the positions in which it was found. In coal-fields barium is a frequent source of ferrous sulphate and of sulphuric acid is found in the iron pyrites in the beds of coal and shale. And I suggested that the constant occurrence of fine veins of calcium sulphate throughout the sandstone of the Nottingham district would account for a sulphate finding its way into the water which had been in contact with the rock. But in the Nottingham district all evidence of barium chloride in solution was wanting.

The occurrence of barium chloride in water from an artesian boring at Ilkeston has, however, recently been pointed out by Mr. John White, and he has described the nature of the strata through which the boring passed, and the results obtained by him in the chemical examination of the water, in *The Analyst* (February, 1899). The Ilkeston boring has been made in the immediate neighbourhood of the Brancote and Stapleford sandstone which contains the large proportion of barium sulphate. Since the barium chloride is found to the extent of 40·7 parts per 100,000 in the water from this boring, and seems to be a normal constituent of the water, it would appear that soluble barium salts are still abundant in the district, and may therefore have given rise to the deposition of the barium sulphate in the original sand beds. The crystallisation of the sulphate around the sand grains would then cause it to act as a compact insoluble cementing material.

It is worthy of note that one of the samples of water from the boring contained a small amount of barium in the presence of a large amount of sodium carbonate; in this case the barium must therefore itself have been present as bicarbonate.

Water containing barium chloride to the extent of about 9 grains per 100,000 has recently been found at Llangammarch, in Breconshire.

Since the publication of my original paper on the occurrence of barium sulphate in the Bramcote sandstone, I have continued my examination of samples of sandstone from the basement of the pebble beds of the Bunter, with the object of ascertaining whether the occurrence of barium, either as sulphate or in other forms of combination, was characteristic of the sandstones of that geological period. I have thus far failed to find any similar rock to that at Brancote, and it therefore seems probable that the occurrence of barium sulphate, although it extends over a very extensive area at Bramcote and Stapleford, must be looked upon as being due to purely local causes.

[*February* 22.—Mr. J. Lomas, in a letter dated 20th instant, draws my attention to a paper read by him and Mr. C. C. Moore before the Liverpool Geological Society, on February 8th, 1898, in which the authors draw attention to the occurrence of large proportions of crystallised barium sulphate in triassic sandstones at Prenton and Bidston. Mr. Lomas had previously mentioned the presence of the sulphate in the Bidston sandstone thirteen years ago in a paper to the above Society.

In different specimens of the sandstone the percentage of the sulphate varied from 12·4 to 33·8 per cent. It is colourless and highly crystalline, and is adherent to the sand grains in such a way as to show that it has been deposited *in situ* subsequently to the sand grains. Mr. Lomas states that the occurrence of barytes in the trias is fairly common, and mentions the following localities in which its presence is well known:—Beeston, Alderley Edge, Oxton, Storeton, and Peakstones Rock, Alton. The sulphate is also stated to occur at West Kirby, in Cheshire, and elsewhere as a joint filling, the joints often standing out from the surface of the rock, owing to the resistance of the sulphate to weathering].—F. C.

* A Paper read before the Royal Society, February 23, 1899.

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MICROSCOPIC DETECTION OF THE PERCHLORATE IN CHILI SALTPETRE.

By M. VAN BREUKELEVEEN.

According to Behrens when we treat the solution of a perchlorate with chloride of rubidium, a precipitate of perchlorate of rubidium is formed in the form of rhombohedric crystals; it is only slightly soluble. It is on this reaction that the author bases a method enabling him to detect 0·6 per cent of perchlorate of potash in the saltpetre.

Ten grms. of saltpetre are dissolved in 10 c.c. of boiling water, add 50 c.c. of 95 per cent alcohol and boil, allow to cool for one or two hours. Decant the clear liquid, evaporate to dryness, and take up the residue with as small as possible a quantity of water. On this solution we try Behrens's reaction. It must be very slightly coloured by means of a drop of permanganate of potash, and one drop of the liquid is placed under the microscope, in order to search for the characteristic crystals of the perchlorate of rubidium.

It is essential that the solution should be hardly coloured rose-colour, or else the crystals of perchlorate of rubidium might be confounded with those of permanganate of rubidium, which are of a deep red colour.—*Chem. Zeit.*, 1898, p. 145.

ON THE REDUCIBILITY OF METALLIC OXIDES.

By HENRI HELIER.

At one of the recent meetings of the Soc é.é Chimique MM. Wyrouboff and Verneuil showed that the oxides of the rare earths polymerise with great facility, and called attention to the fact that many oxides of the ordinary metals behave in the same manner, giving polymers of the general formula $(R_nO_p)_q$, which, far from having q times the basicity of the oxide R_nO_p, are often neutral or even acid. I share their views entirely on this subject. It is for this reason that the oxide of iron, Fe_2O_3, which has not been heated above 450° C. is basic, since it gives ferric sulphate on dissolving in sulphuric acid, while after being heated to above a dull red heat it becomes neutral and is polymerised. It then no longer dissolves in sulphuric acid. Its formula should now be written $(Fe_2O_3)_n$.

It often happens that reactions, impossible with the polymerised molecule, are possible under the same conditions with the simple molecule.

For example, let us heat litharge to the temperature of 350° in a current of hydrogen. The solid body becomes brown and loses oxygen, but the reduction is never complete. As we increase the temperature the loss of oxygen becomes greater and greater, and that in a continuous manner; this, by the way, makes it apparent to me that the existence of a suboxide is hardly possible.

If instead of the oxide we have to do with a neutral compound such as the carbonate, the reduction by means of hydrogen is then perfectly easy; at a temperature of 325° and upwards it is complete.

From this I think we may draw the following conclusions:—

1. That litharge is a polymer with the formula $(PbO)_n$, which, when reduced by hydrogen, decomposes successively into $Pb_1(PbO)_{n-1}$, then to $2Pb_1(PbO)_{n-2}$, &c.

2. That the simple type PbO should be sought for in the only neutral salts, such as the carbonate.

3. That the reduction of the simple oxide PbO is infinitely more easy to effect than the reduction of the polymerised molecule.

If, however, from these few experiments with oxide of lead, we could rise to more general considerations, we should say that the reduction of metallic oxides should always be considered to be more easy when starting with neutral salts. This view is corroborated by the results of experiments; we know, in fact, that in metallurgy we always make carbon react on the neutral mixtures obtained by adding silica to the basic mineral, or carbonate of lime to the acid mineral; these are neutral mixtures which, under the influence of temperature, give birth to neutral compounds.—*Bull. Soc. Chim.*, Series 3, vol. xxi.-xxii., No. 2.

ESTIMATION OF THE PERCHLORATE IN CHILI SALTPETRE.

By C. AHRENS and P. HETT.

The following method will be found sufficiently rapid and exact for commercial analysis:—

Twenty grms. of the well powdered substance are placed in a platinum crucible and moistened with 2 or 3 c.c. of a cold saturated solution of carbonate of soda, add 1 grm. of binoxide of manganese free from chlorine and evaporate to dryness. The mass is brought to fusing point, and the crucible, which must be well covered, is kept at a red heat for fifteen minutes. The product of this fusion is, after cooling, dissolved in 100 c.c. of boiling water, the solution is cooled and made up to 250 c.c.; of this when filtered 50 c.c. are taken (equal to 4 grms. of the sample), acidulate with 10 or 15 c.c. of nitric acid of 1·2 density, then add a 1 per cent solution of permanganate of potash until the red colour lasts for at least a minute. We then add ferrous sulphate and titrate the solution by Volhard's method.

The chlorine is also determined in 4 grms. of the sample by Volhard's method. From the difference between the number of c.c. of decinormal argentic solution employed after fusion, and the number obtained before fusion we calculate the chlorine which exists in the saltpetre in the state of perchlorate.

The addition of carbonate of soda before fusion is simply to prevent the partial volatilisation of the hydrochloric acid. The addition of the binoxide of manganese facilitates the decomposition of the perchlorate; and finally the treatment with permanganate has for its object the elimination of the nitrous acid, and the transformation into iodate, of the small quantity of iodine which is present in the sample in the state of iodide.—*Zeits. für. Offentl. Chem.*, iv., p. 445.

ON A NEW METHOD FOR THE ELECTROLYTIC PRODUCTION OF CHLORATES, BROMATES, IODATES, AND HYPOCHLORITES.

By WILHELM VAUBEL.

According to the process patented by Schuckert and Co. (German patent, No. 13.536), relating to the electrolysis of the alkaline chlorides, the return, in chlorate, is augmented when the liquid in the anodic compartment is kept alkaline by the addition of 1 to 5 per cent of carbonate of potash or soda. Under these conditions we not only prevent the formation of a caustic alkali at the point of contact of the easily attacked carbon anodes, but we also obtain a greater return of chlorine, since the electric conductivity of the caustic alkalis is decidedly higher than that of the corresponding chlorates and carbonates.

In making further researches I found that, on the one hand, by making use of a diaphragm, and on the other hand using bicarbonate of soda as the anodic solution, and the alkaline chloride as the cathodic solution, all the

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chlorine which is carried to the anode is transformed into chlorate, and not a trace of chloride is formed. The reaction may be expressed by the following equation:—

$$\overset{-}{\underset{+}{NaCl}} + \overset{-}{\underset{+}{NaHCO_3}} = 6NaClO_3 + 6\overset{+}{\underset{-}{CO_2}} + 6Na + 3H_2O.$$

In this equation the bodies disengaged at the anode are marked +, and those carried to the cathode −.

It remains to determine in what manner the percarbonic acid formed participates in this reaction through the intermediate compounds.

In this equation, the same as in all other methods for the electrolytic production of chlorates, six atoms of sodium are disengaged, for one molecule of chlorate formed:—$Cl_6 + 6NaOH = 5NaCl + NaClO_3 + H_2O$. But in my process this sodium can be recovered in the state of caustic soda. Further, at the anode we obtain a chlorate which is almost entirely free from chloride. As for the carbonic acid which is given off, it can be collected in a solution of carbonate of soda forming bicarbonate.

The working conditions remain the same as in the ordinary methods. The electrolysis is carried on at from 60° to 70° C., that is to say at a temperature which is not high enough to decompose the bicarbonate to any appreciable extent. The density of the current may vary from 5 to 10 ampères per square decimetre. It may be mentioned that the greater the current the higher the return. In the greater number of my experiments the electromotive force was kept between 4 and 5 volts; in some it was a little higher on account of the greater resistance of the diaphragm.

The anodic solution consisted of a saturated solution of bicarbonate of soda or potash. When the action of the current represented 4 ampère-hours, 5 grms. of bicarbonate of soda were added per 100 c.c. of solution; this addition was decreased a little towards the end of the operation. The electrolysis gave a solution of 6·5 grms. of chlorate of soda for every 7·5 grms. of bicarbonate of soda. We found that it was useless to try to increase this return by prolonging the action of the current, for then the useful effect of the current diminishes with great rapidity. At the commencement of the electrolysis the cathode compartment contained a saturated solution of sea salt. At the end of the electrolysis it contained a 10 per cent solution of caustic soda with a very small quantity of sea salt.

The quantities of chlorate of soda obtained are the following:—

For	2	ampère-hours	..	0·36 grm.	$NaClO_3$.
,,	6	,,	..	1·03	,,
,,	10	,,	..	2·62	,,
,,	14	,,	..	4·23	,,
,,	18	,,	..	5·84	,,
,,	26	,,	..	7·92	,,
,,	34	,,	..	11·22	,,
,,	38	,,	..	12·90	,,

According to Oettel's researches (*Zeits. Elect*, 1895, p. 354), by using an electromotive force of 3·3 volts and admitting a useful current effect of 52 per cent, we should obtain a return of 88·14 grms. of chlorate of potash per effective horse-power-hour of 746 watts. The production of 1 kilogrm. of chlorate of potash would therefore require, under the same working conditions, an electromotive force of 11·5 volts. But it must be remembered that Oettel operated on a slightly alkaline solution of the chloride, and without a diaphragm.

In Gall and Montlaur's process, which is now being carried on commercially, a diaphragm is used and the alkaline solution is added at regular intervals to the anodic compartment. The electromotive force being the same as in my process, we will here admit that the production of 88·14 grms. of chlorate of potash corresponds to an expenditure of 1003·5 watts, supposing the density of the current is the same as that recommended by Oettel. Now by my process the production of 88·14 grms. of chlorate of potash only requires the expenditure of 951·91 watts. And further I must repeat that I obtain a solution of caustic alkali at the cathode. If we use carbonate of soda or carbonate of potash, which are always easily transformed into bicarbonate by the carbonic acid given off during the electrolysis, it can be easily seen that my process compares very favourably with those actually in use.

The working conditions are the same for chlorate of soda and for chlorate of potash. By means of this process we can equally well prepare the alkaline bromates and iodates in a very satisfactory state of purity. I must remark that I have not tried any experiments to determine whether this method gives rise to the formation of more or less large quantities of perchlorates, perbromates, &c. By working at a low temperature we obtain hypochlorites instead of chlorates. But here again the product obtained is almost entirely free from chloride. The hypochlorite solutions thus obtained are less stable on heating; it would therefore seem that this stability depends on the presence of the chloride.

The bicarbonates of soda and potash cannot be replaced by the corresponding carbonates, or chlorides will be formed at the same time as the chlorates. Nor can the bicarbonates of soda and potash be replaced by that of ammonia, as it is decomposed by heat; further electrolysis in the cold under these conditions gives chloride of nitrogen.

Before closing I will mention a few experiments I made in which I endeavoured to utilise the oxidising properties of the bicarbonate when submitted to electrolysis.

1. Ferrocyanide of potassium is easily transformed into ferricyanide with the formation of Prussian blue at the anode.

2. Hydrate of baryta is not oxidised; but, on the contrary, hydrate of chromium is easily; anyhow in this case the useful effect of the current is only 3 per cent, while Hœussermann obtained a useful effect of 47 per cent by electrolysing hydrate of chromium in suspension in an excess of caustic soda.

3. Experiments made with a view to the electrolytic preparation of fluorates by the same method gave no results.—*Chemiker Zeitung*, 1898, No. 34, p. 331.

THE ESTIMATION OF BORIC ACID.*

By F. A. GOOCH AND LOUIS CLEVELAND JONES.

(Concluded from p. 100).

The Use of Calcium Oxide as a Retainer (continued).

If we take into consideration, therefore, the inevitable inaccuracy and inconvenience of Thaddeeff's proposal, it cannot be regarded as a desirable substitute for the process according to which boric acid is absorbed and retained for weighing with calcium oxide, especially since the difficulties in the way of getting constant weights of that substance are by no means insuperable.

Thus the following table shows the series of weights taken in several experiments in bringing calcium oxide to a constant weight in a 50 c.m.³ platinum crucible ignited over a blast lamp, as well as the weight taken after adding a known amount of standard boric acid solution to the slaked oxide, evaporating, and igniting. The results recorded are those of experiments made on days not moist beyond the average, and with the greatest care to approach the limit of accuracy with which calcium oxide and the boric acid held thereby can be weighed under ordinarily favourable conditions. The first weight of calcium oxide recorded under each experiment was taken after a strong ignition over the blast lamp for about one-half hour. The succeeding weights were taken after similar ignition

* Contributions from the Kent Chemical Laboratory of Yale University. From the *American Journal of Science*, vol. vii, 1899.

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of five minutes. In all cases the crucible was left to stand a definite period in a sulphuric acid desiccator, and, after the approximate value had once been obtained, the weights of the preceding weighing were replaced on the balance before the crucible was taken from the desiccator. The average of the weights bracketed is the weight taken as constant for the calculations.

	CaO taken.	B_2O_3 taken.	CaO+B_2O_3 taken.	CaO+B_2O_3 found.		Error.
	Grm.	Grm.	Grm.	Grm.		Grm.
1.	0·9505 0·9493 0·9493	0·9493	0·2095	1·1588	1·1590 1·1591	1·1591	+0·0003
2.	1·1319 1·1317 1·1313 1·1315	1·1315	0·2150	1·3465	1·3499 1·3474 1·3475 1·3276	1·3475	+0·0010
3.	0·8028 0·8025 0·8024	0·8024	0·1184	0·9208	0·9205 0·9206 0·9206	0·9206	+0·0002
4.	2·6980 2 6975 2 6973 2 6973	2·6973	0·2073	2·9046	2·9043 2·9049 2 9044	2·9048	+0·0002

Obviously calcium oxide may be weighed with accuracy, with or without boric acid; but the fact remains that a less hygroscopic absorbent—one requiring less care in the handling—is to be desired.

The Use of Sodium Tungstate as a Retainer.

In searching for a suitable material of less hygroscopicity to replace calcium oxide as a retainer for boric acid, we have found that sodium tungstate, fused with a slight excess of tungstic acid over that contained in the normal tungstate to insure its freedom from carbonate), answers this purpose excellently. This substance is definite in weight, not hygroscopic, soluble in water, and recoverable in its original weight after evaporation and ignition. To test its value as a retainer for boric acid, portions of it—4 to 7 grms.—were fused and weighed in a 50 c.m.³ crucible, the tungstate was dissolved in water, and to it was added a known amount of a standard solution of boric acid. After diluting, mixing, evaporating, and fusing the residue, the increase in weight should represent the boric anhydride held by the tungstate. The results of the accompanying table show how accurately the boric acid is retained under these conditions. In Experiments 3 to 7 the tungstate, after its first weighing, was dissolved, transferred to a larger platinum dish, and mixed therein with the boric acid. After evaporation to a suitable volume this solution of tungstate and boric acid was transferred to the original crucible for final evaporation and ignition.

$Na_2WO_4+WO_3$ taken.	B_2O_3 taken.	B_2O_3 found.	Error in B_2O_3.
Grm.	Grm.	Grm.	Grm.
6·5416	0·1784	0·1771	−0·0013
7·3134	0·1786	0·1773	−0·0013
5 5003	0·0950	0·0952	+0·0002
4·1394	0 0944	0·0944	0·0000
7·5037	0 2148	0·2149	+0·0001
4·7744	0·2718	0·2702	−0·0016
6·6470	0 2503	0·2487	−0·0016

It is plain that, though the sodium tungstate does not hold the boric acid with absolute accuracy, the errors are not unreasonable, −0·0008 grm. in the mean. Upon substituting the tungstate for calcium oxide as a retainer in the distillation process, the results were likewise highly favourable.

We used by preference the apparatus originally proposed, excepting that the Erlenmeyer flask used as a receiver is fitted tightly to the condenser and trapped with water bulbs. The retort is made very easily from a 150 c.m.³ pipette, and has the special advantage that particles of the residue spattering during distillation are easily washed from the walls of the vessel by a slight rotary motion of the retort. It was found that special care should be taken to give the tungstate ample time for contact with the distillate before exposing the latter to atmospheric evaporation. The distillate was received, therefore, in a dilute solution of sodium tungstate placed in the receiver, cooled by ice and trapped with water, and the mixture was well stirred, allowed to stand one-half hour, evaporated to small volume in a large dish, and transferred to the crucible in which the tungstate had been originally weighed. After thorough drying, the residue was ignited to fusion and weighed. When acetic acid was employed in the retort, care was taken in the ignition to expose the fused mass freely to the air (by causing it to flow upon the sides of the crucible) until the colour of the cooled tungstate was white, in order that the reducing effect of the acetate might be eliminated. In the experiments recorded in the following table the tungstate was used in the receiver to retain the boric acid distilled as usual with methyl alcohol, from the borates treated with acetic acid, nitric acid, or sulphuric acid, in amounts regulated by the use of phenolphthalein as an indicator.

$Na_2WO_4+WO_3$ taken.	B_2O_3 taken.	B_2O_3 found.	Error.
Grm.	Grm.	Grm.	Grm.
		With Nitric Acid.	
8·5516	0·1582	0·1572	−0·0010
4·9639	0·1329	0·1323	−0·0006
8·0033	0·1267	0·1256	−0·0011
		With Acetic Acid.	
4·9658	0·1434	0·1418	−0·0016
6·0289	0·1431	0·1433	+0·0002
4·6797	0·1589	0·1587	−0·0002
4·0013	0·1433	0·1422	−0·0011
		With Sulphuric Acid.	
6·3439	0·1582	0·1579	−0·0003
8 8227	0·1582	0·1577	−0·0005
10·1516	0·1265	0·1264	−0·0001
6·5738	0·1392	0·1390	−0·0002

Excessive use of acid is disadvantageous, and this is especially true in the case of sulphuric acid; for if this acid is carried over with the methyl alcohol, as it is at 100° if present in appreciable excess, a part of it, at least, is held permanently by the tungstate to increase the apparent weight of the boric acid to be estimated.

The manipulation of the tungstate presents no difficulties, and the results obtained by its use are reasonably accurate.

ON THE

SEPARATION OF IRON FROM ZIRCONIUM AND CERTAIN OTHER ALLIED METALS.*

By J. MERRITT MATTHEWS.

(Concluded from p. 99).

As thorium, cerium, and titanium belong to the same group as zirconium, and form corresponding hydrated oxychlorides insoluble in ether, the same method was applied in the separation of iron from these metals as with zirconium, and very good results were obtained. The method was carried out in every particular as already described, and was also extended to include lanthanum, neodymium, and praseodymium, as their hydrated chlorides were found to be insoluble in ether.

* *Journal of the American Chemical Society*, xx., No. 11, Nov., 1898.

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Thorium from Iron.

The thorium salt used was the chloride, and its analysis gave 60·79 per cent thorium dioxide, and was not appreciably contaminated with iron, so no correction was necessary in the percentages found.

I. 0·5608 grm. thorium tetrachloride with 0·2246 grm. ferric chloride gave :—
0·3418 grm. thorium dioxide = 60·95 per cent thorium dioxide.
0·0657 grm. ferric oxide = 29·25 per cent ferric oxide.

II. 0·2681 grm. thorium tetrachloride with 0·4625 grm. ferric chloride gave :—
0·1628 grm. thorium dioxide = 60·72 per cent thorium dioxide.
0·1364 grm. ferric oxide = 29·53 per cent ferric oxide.

III. 0·5072 grm. thorium tetrachloride with 0·3217 grm. ferric chloride gave :—
0·3075 grm. thorium dioxide = 60·63 per cent thorium dioxide.
0·0952 grm. ferric oxide = 29·59 per cent ferric oxide.

IV. 1·0368 grm. thorium tetrachloride with 0·7241 grm. ferric chloride gave :—
0·6318 grm. thorium dioxide = 60·94 per cent thorium dioxide.
0·2137 grm. ferric oxide = 29·51 per cent ferric oxide.

V. 0·1193 grm. thorium tetrachloride with 0·6976 grm. ferric chloride gave :—
0·0720 grm. thorium dioxide = 60·35 per cent thorium dioxide.
0·2062 grm. ferric oxide = 29·58 per cent ferric oxide.

	Used.	Found. I.	II.	III.	IV.	V.
Ferric oxide	29·44	29·25	29·53	29·59	29·51	29·58
Thorium dioxide ..	60·79	60·95	60·72	60·63	60·94	60·35

Cerium from Iron.

Cerium chloride was used, and its analysis gave 61·11 per cent cerium dioxide.

I. 0·1098 grm. cerium chloride with 0·3510 grm. ferric chloride gave :—
0·0669 grm. cerium dioxide = 60·93 per cent cerium dioxide.
0·1044 grm. ferric oxide = 29·74 per cent ferric oxide.

II. 0·1930 grm. cerium chloride with 0·2574 grm. ferric chloride gave :—
0·1178 grm. cerium dioxide = 61·04 per cent cerium dioxide.
0·0758 grm. ferric oxide = 29·45 per cent ferric oxide.

III. 0·2240 grm. cerium chloride with 0·2642 grm. ferric chloride gave :—
0·1367 grm. cerium dioxide = 61·03 per cent cerium dioxide.
0·0784 grm. ferric oxide = 29·67 per cent ferric oxide.

IV. 0·7532 grm. cerium chloride with 0·1024 grm. ferric chloride gave :—
0·4598 grm. cerium dioxide = 61·05 per cent cerium dioxide.
0·0301 grm. ferric oxide = 29·39 per cent ferric oxide.

V. 0·1262 grm. cerium chloride with 0·8436 grm. ferric chloride gave :—
0·0774 grm. cerium dioxide = 61·33 per cent cerium dioxide.
0·2489 grm. ferric oxide = 29·52 per cent ferric oxide.

	Used.	Found. I.	II.	III.	IV.	V.
Ferric oxide	29·44	29·74	29·45	29·67	29·39	29·52
Cerium dioxide ..	61·11	60·93	61·04	61·03	61·05	61·33

Titanium from Iron.

Titanium chloride was the salt used, and on analysis this gave 57·17 per cent titanium dioxide.

I. 0·1060 grm. titanium chloride with 0·2224 grm. ferric chloride gave :—
0·0604 grm. titanium dioxide = 56·98 per cent titanium dioxide.
0·0660 grm. ferric oxide = 29·68 per cent ferric oxide.

II. 0·2588 grm. titanium chloride with 0·2508 grm. ferric chloride gave :—
0·1474 grm. titanium dioxide = 56·95 per cent titanium dioxide.
0·0736 grm. ferric oxide = 29·35 per cent ferric oxide.

III. 0·6532 grm. titanium chloride with 0·1086 grm. ferric chloride gave :—
0·3728 grm. titanium dioxide = 57·08 per cent titanium dioxide.
0·0318 grm. ferric oxide = 29·28 per cent ferric oxide.

IV. 0·3549 grm. titanium chloride with 0·7643 grm. ferric chloride gave :—
0·2033 grm. titanium dioxide = 57·28 per cent titanium dioxide.
0·2253 grm. ferric oxide = 29·48 per cent ferric oxide.

V. 0·1083 grm. titanium chloride with 0·9212 grm. ferric chloride gave :—
0·0617 grm. titanium dioxide = 56·97 per cent titanium dioxide.
0·2720 grm. ferric oxide = 29·53 per cent ferric oxide.

	Used.	Found. I.	II.	III.	IV.	V.
Ferric oxide	29·44	29·68	29·35	29·28	29·48	29·53
Titanium dioxide .	57·17	56·98	56·95	57·08	57·28	56·97

Lanthanum from Iron.

The lanthanum chloride used in the analyses gave 50·20 per cent lanthanum oxide, La_2O_3.

I. 0·2968 grm. lanthanum chloride with 0·1465 grm. ferric chloride gave :—
0·1485 grm. lanthanum oxide, La_2O_3, = 50·03 per cent lanthanum oxide.
0·0435 grm. ferric oxide = 29·69 per cent ferric oxide.

II. 0·4541 grm. lanthanum chloride with 0·7105 grm. ferric chloride gave :—
0·2274 grm. lanthanum oxide, La_2O_3, = 50·08 per cent lanthanum oxide.
0·2098 grm. ferric oxide = 29·53 per cent ferric oxide.

III. 0·1079 grm. lanthanum chloride with 0·6514 grm. ferric chloride gave :—
0·0539 grm. lanthanum oxide, La_2O_3, = 49·95 per cent lanthanum oxide.
0·1926 grm. ferric oxide = 29·57 per cent ferric oxide.

IV. 0·7525 grm. lanthanum chloride with 0·1024 grm. ferric chloride gave :—
0·3769 grm. lanthanum oxide, La_2O_3, = 50·09 per cent lanthanum oxide.
0·0304 grm. ferric oxide = 29·68 per cent ferric oxide.

V. 0·5048 grm. lanthanum chloride with 0·5025 grm. ferric chloride gave :—
0·2539 grm. lanthanum oxide, La_2O_3, = 50·30 per cent lanthanum oxide.
0·1485 grm. ferric oxide = 29·55 per cent ferric oxide.

	Used.	Found. I.	II.	III.	IV.	V.
Ferric oxide	29·44	29·69	29·54	29·57	29·68	29·55
Lanthanum oxide, La_2O_3	50·20	50·03	50·08	49·95	50·09	50·30

Praseodymium from Iron.

The salt used was praseodymium nitrate, and its analysis gave 43·33 per cent praseodymium oxide, Pr_2O_3.

I. 0·5308 grm. praseodymium nitrate with 0·4245 grm. ferric chloride gave :—
0·2293 grm. praseodymium oxide, Pr_2O_3, = 43·20 per cent praseodymium oxide.

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0·1261 grm. ferric oxide = 29·70 per cent ferric oxide.

II. 0·5090 grm. praseodymium nitrate with 0·3596 grm. ferric chloride gave :—

0·2198 grm. praseodymium oxide, Pr_2O_3, = 43·18 per cent praseodymium oxide.

0·1064 grm. ferric oxide = 29·59 per cent ferric oxide.

III. 0·1085 grm. praseodymium nitrate with 0·7240 grm. ferric chloride gave :—

0·0465 grm. praseodymium oxide, Pr_2O_3, = 42·86 per cent praseodymium oxide.

0·2139 grm. ferric oxide = 29·54 per cent ferric oxide.

IV. 0·6849 grm. praseodymium nitrate with 0·1096 grm. ferric chloride gave :—

0·2960 grm. praseodymium oxide, Pr_2O_3, = 43·33 per cent praseodymium oxide.

0·0323 grm. ferric oxide = 29·43 per cent ferric oxide.

V. 0·2532 grm. praseodymium nitrate with 0·2485 grm. ferric chloride gave :—

0·1092 grm. praseodymium oxide, Pr_2O_3, = 43·13 per cent praseodymium oxide.

0·0735 grm. ferric oxide = 29·58 per cent ferric oxide.

	Used.	Found. I.	II.	III.	IV.	V.
Ferric oxide	29·44	29·70	29·59	29·54	29·43	29·58
Praseodymium oxide, Pr_2O_3	43·33	43·20	43·18	42·86	43·22	43·13

Neodymium from Iron.

Neodymium nitrate was used, and its analysis gave 42·20 per cent neodymium oxide, Ne_2O_3.

I. 0·1763 grm. neodymium nitrate with 0·4286 grm. ferric chloride gave :—

0·0740 grm. neodymium oxide, Ne_2O_3, = 41·97 per cent neodymium oxide.

0·1261 grm. ferric oxide = 29·42 per cent ferric oxide.

II. 0·6389 grm. neodymium nitrate with 0·1842 grm. ferric chloride gave :—

0·2688 grm. neodymium oxide, Ne_2O_3, = 42·07 per cent neodymium oxide.

0·0540 grm. ferric oxide = 29·32 per cent ferric oxide.

III. 0·7246 grm. neodymium nitrate with 0·7562 grm. ferric chloride gave :—

0·3051 grm. neodymium oxide, Ne_2O_3 = 42·11 per cent neodymium oxide.

0·2229 grm. ferric oxide = 29·48 per cent ferric oxide.

IV. 0·1545 grm. neodymium nitrate with 0·2046 grm. ferric chloride gave :—

0·0645 grm. neodymium oxide, Ne_2O_3, = 41·75 per cent neodymium oxide.

0·0610 grm. ferric oxide = 29·81 per cent ferric oxide.

V. 0·2081 grm. neodymium nitrate with 0·7680 grm. ferric chloride gave :—

0·0869 grm. neodymium oxide, Ne_2O_3, = 41·76 per cent neodymium oxide.

0·2271 grm. ferric oxide = 29·57 per cent ferric oxide.

	Used.	Found. I.	II.	III.	IV.	V.
Ferric oxide	29 44	29·42	29·32	29·48	29 81	29·57
Neodymium oxide, Ne_2O_3	42·20	41·97	42·07	42·11	41·75	41·76

The praseodymium and neodymium salts existing originally as nitrates, were evaporated to dryness with hydrochloric acid in order to convert them into the chloride form.

General Remarks.

Gooch and Havens, in the *American Journal of Science* for December, 1896 (see also Chemical News, vol. lxxiv., p. 296), describe a method for the separation of aluminum from iron by treatment with anhydrous ether saturated with hydrochloric acid gas. The hydrated chloride of aluminum remains insoluble, whereas the ferric salt is completely dissolved. This method is practically the same as the one herein described for the separation of iron from zirconium and the other rare earths; but the results of this present research were mostly obtained in October and November, 1896, before the writer was aware of the contemporaneous work of Gooch and Havens. These latter writers also describe a separation of aluminum from glucinum by the same method (*Am. Journ. Sci.*, August, 1897).

The use of absolute ether may militate somewhat against the practical application of this method to general analytical purposes; since in the case of most of the metals experimented upon, very good separations are already known which do not require the use of a reagent both difficult and unpleasant to manipulate. This method, however, is especially recommended for the separation of iron from zirconium, the separations of the other metals being only tried as a matter of interest through the analogy existing between those metals and zirconium. A point, however, which may prove of practical importance, and which it is most desirable to emphasize here, is that by carefully following out the procedure herein described, zirconium oxychloride and dioxide may be easily and quickly prepared perfectly free from iron. This fact may be of considerable importance and utility in the preparation of zirconium compounds for use in atomic weight determinations, where a high degree of purity is absolutely necessary in order to obtain authentic results.

THE

DETERMINATION OF SULPHUR IN ASPHALT.*

By E. H. HODGSON.

The numerous articles recently published on the analysis and chemistry of asphalts, and the wide range of opinion as to the relative values of the different methods in use for the determination of sulphur, have led me to make a comparison of results on some typical asphalts.

Dr. E. H. Miller, through the kindness of Mr. A. W. Dow, of Washington, was enabled to secure samples, the sources and natures of which were known. The samples were labelled Trinidad Lake, Trinidad Crude, Trinidad Lake Refined, Cuban Crude, Alcatraz Crude, and California Crude, and were described by Mr. Dow as follows :—

Trinidad Lake.—Asphalt from the lake on the island of Trinidad, imported by Barber Asphalt Co. for paving.

Trinidad Crude. — Crude asphalt from Hadley's Diggings, about one mile from Trinidad Lake. It is known as "iron pitch," being the hardest asphalt found in Trinidad.

Trinidad Lake Refined.—This is crude Trinidad Lake asphalt melted up to drive out the water.

Alcatraz Crude.—From Ventura Co., California, used by the Alcatraz Asphalt Co. for paving, after the addition of liquid asphalt.

California Crude.—From Kern Co., California, used by the Standard California Asphalt Co. for paving, after the addition of liquid asphalt.

Sample "Trinidad Lake" was found to lose water very rapidly, so it was heated to about 60° C. (not sufficient to melt it) and then remained constant.

The samples were ground as fine as possible in a mortar, and then placed in glass bottles fitted with tight corks. From these bottles average samples were taken and kept in test-tubes for use.

Heating with Strong Nitric Acid in a Sealed Tube—Carius's Method.

The tubes were made in the usual way from heavy glass

* Contributions from the Havemeyer Laboratories of Columbia University. From the *Journal of the American Chemical Society*, xx., No. 11.

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tubing. Two determinations were made on each sample. One on ½ grm. and one on ¾ grm. A general description of the method is as follows:—One-half grm. of asphalt is introduced into the bottom of the tube, and 15 c.c. of fuming nitric acid (1·60 sp. gr.) is poured upon it. The open end of the tube is then drawn out into a thick-walled fine-calibre tube, but not sealed. The tube is then heated for about six hours in a water-bath kept at 80—90° C. Then 5 c.c. more acid are added, the tube is sealed, and heated in a guarded furnace at a temperature of about 150° C. for from four to five hours. Allow the tube to cool, then open and re-seal, and re-heat for from two to four hours at a temperature of 180—200° C. Cool, open, and remove the liquid and residue into a No. 2 beaker. Dilute with water, filter, and wash. If the residue contains anything but sand it is saved and treated separately. The filtrate is evaporated to dryness on the water-bath, adding a piece of solid sodium hydroxide. The nitric acid is driven out by repeated evaporation of the solution, with the addition of hydrochloric acid, and the silica dehydrated in an air-bath at 110—115° C. Cool the dehydrated mass, add 2 to 3 c.c. of hydrochloric acid and 100 c.c. of water, stir well, filter, and wash well with hot water. Dilute the filtrate to about 200 c.c., heat to boiling, and while boiling add 20 c.c. of barium chloride (20 per cent solution), drop by drop, from a burette, at the rate of about a drop a second. Stir all the time. Boil the solution about ten minutes, and allow it to stand twenty-four hours. Filter, wash with hot water, and ignite. Treat with sulphuric acid, and re-ignite. Then cool and weigh the barium sulphate. A pure white product was obtained, and the precipitate did not run through the filter.

The residue from the sealed tube, if not thoroughly oxidised, is fused with 6 grms. of mixed carbonates and 1 grm. of potassium nitrate. The fusion is dissolved in water and hydrochloric acid. The nitrates are destroyed by evaporating with the addition of hydrochloric acid, and the silica dehydrated as before. Filter off the silica and wash. Then determine the sulphuric acid in the filtrate as before described.

When ¾ grm. of asphalt was used, 25 c.c. of fuming nitric acid were employed instead of 20 c.c.

The following results were obtained:—

	Weight of barium sulphate. Grm.	Sulphur. Per cent.
Trinidad Lake.		
One-half grm.	0·1526	4·192
Residue	0·0051	0·140
		4·332
Three-fourths grm.	0·2238	4·10
Residue	0·0068	0·18
		4·28
Trinidad Crude.		
One-half grm.	0·1249	3·400
Residue	0·0034	0·086
		3·486
Three-fourths grm.	0·1720	3·148
Residue	0·0106	0·19
		3·338
Trinidad Lake Refined.		
One-half grm.	0·1585	4·35
Residue	—	—
		4·35
Three-fourths grm.	0·2160	4·21
Residue	0·0137	0·25
		4·46
Cuban Crude.		
One-half grm.	0·1315	3·61
Residue	—	—
		3·61
Three-fourths grm.	No results.	
Alcatraz Crude.		
One-half grm.	0·1839	5·05
Residue	0·0195	0·54
		5·59
Three-fourths grm.	0·2749	5·12
Residue	0·0294	0·46
		5·58
California Crude.		
One-half grm.	0·2589	7·11
Residue	0·0145	0·398
Three-fourths grm.	No results.	

Deflagration Method—S. F. and H. E. Peckham.

A porcelain crucible is heated to a dull red heat, and *small* amounts of a mixture of 1 grm. finely ground asphalt, 8 grms. of potassium nitrate, and 8 grms. of mixed sodium and potassium carbonates added from time to time, just keeping the material in the crucible melted. When all of the mixture has been added, heat to perfect fusion with a blast lamp, and cool. Dissolve the fusion in 20 c.c. hydrochloric acid and 40 c.c. of water, and wash the crucible well with hot water. The solution is evaporated down to dryness, dehydrated at 110—115°, the silica filtered off, and the sulphuric acid determined in the filtrate as before. The results are as follows:—

No.	Weight of barium sulphate. Grm.	Sulphur. Per cent.
Trinidad Lake.		
1.	0·2770	3·804
2.	0·2689	3·68
Trinidad Crude.		
1.	0·2443	3·37
2.	0·2359	3·24
Trinidad Lake Refined.		
1.	0·2634	3·62
2.	—	—
Cuban Crude.		
1.	0·2009	2·76
2.	0·2052	2·82
Alcatraz Crude.		
1.	0·3054	4·19
2.	0·2773	3·81
California Crude.		
1.	0·4376	6·50
2.	—	—

Sodium Peroxide Method.

Place 1 grm. of the fine asphalt in the bottom of a large nickel crucible. Cover with a layer of about 4 grms. of mixed carbonates and about 1 grm. of solid sodium hydroxide. Cover the crucible and heat gently until the gases are driven off. Then raise the heat and add small amounts of sodium peroxide from time to time, until no further action is noticed on the addition of fresh Na_2O_2. Then, with the blast-lamp, heat to perfect fusion. This takes but a few minutes. Pour as much of the fusion as possible upon the cover of the crucible and cool slowly.

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Place the fusion, crucible, and cover in a casserole containing 50 c.c. hot water, and after thorough digestion on the water-bath, filter off the residue and wash well with hot water. The filtrate is made acid with hydrochloric acid, and evaporated down to dryness, dehydrated at 110—115° C., the silica filtered off, and the sulphuric acid determined in the filtrate as already described. Results by this method :—

Trinidad Lake.

No.	Weight of barium sulphate. Grm.	Sulphur. Per cent.
1.	0·2687	3·69
2.	0·2744	3·77
	Trinidad Crude.	
1.	0·2426	3·33
2.	0·2360	3·25
	Trinidad Lake Refined.	
1.	0·2962	4·07
2.	0·2929	4·02
	Cuban Crude.	
1.	0·2256	3·10
2.	0·2230	3·06
	Alcatraz Crude.	
1.	0·2887	3·97
2.	0·2880	3·96
	California Crude.	
1.	0·4557	6·26
2.	0·4481	6·15

Ignition with Calcined Magnesia—Eschka's Method.

One grm. of finely ground asphalt is intimately mixed with 1 grm. of calcined magnesia and about ½ grm. of dry mixed carbonates is added. Mix well and place in a platinum or porcelain crucible. With the crucible in an inclined position, heat at a dull red heat, stirring every few minutes, until the ash is a dull yellow. Cool, and add about 1 grm. of finely-ground ammonium nitrate, and mix thoroughly. Heat slowly to a dull red, and continue the heating until the ammonium nitrate is entirely decomposed. Cool, extract the mass thoroughly with water (hot water preferred), filter, and wash well. Acidulate the filtrate with hydrochloric acid, and precipitate the sulphuric acid as before described. The results are as follows :—

Trinidad Lake.

No.	Weight of barium sulphate. Grm.	Sulphur. Per cent.
1.	0·2660	3·65
2.	0·2791	3·83
	Trinidad Crude.	
1.	0·2608	3·58
2.	0·2567	3·53
	Trinidad Lake Refined.	
1.	0·2744	3·77
2.	0·2650	3·64
	Cuban Crude.	
1.	0·2020	2·77
2.	0·1941	2·66
	Alcatraz Crude.	
1.	0·3054	4·19
2.	0·3021	4·16
	California Crude.	
1.	0·5011	6·88
2.	0·5109	7·01

The relative accuracy of the different methods is best shown by tabulating the results, as follows :—

	Trinidad Lake.	Trinidad Crude.	Trinidad Lake Refined	Cuban Crude.	Alcatraz Crude.	California Crude.
Sealed tube..	4·33	3·49	4·35	3·61	5·59	7·51
	4·28	3·34	4·46	—	5·57	—
Deflagration.	3·80	3·37	3·62	2·82	4·19	6·50
	3·68	3·24	—	2·76	3·81	—
Peroxide ..	3·69	3·33	4·07	3·10	3·97	6·26
	3·77	3·25	4·02	3·06	3·96	6·15
Eschka's ..	3·65	3·58	3·77	2·77	4·19	6·88
	3·83	3·53	3·64	2·66	4·16	7·01

It would appear, therefore, that the "sealed tube" gives the most accurate results, but on account of the explosion of the tubes and the time required for a determination, it would probably be barred out.

The deflagration method apparently gives low results. It is much shorter than the sealed tube, but longer than either the peroxide or Eschka's method.

Of the latter two, the Eschka's method is perhaps the better, as it requires less time and attention to carry out, and gives about as good results.

The peroxide method is shorter than the deflagration method and about as accurate.

The reagents employed were first tested for sulphur.

	Sulphur. Per cent.
The sodium and potassium carbonate contained	0·005
The sodium peroxide contained	0·003

The rest of the reagents were sulphur-free or contained but the merest trace.

PROCEEDINGS OF SOCIETIES.

PHYSICAL SOCIETY.

Ordinary Meeting, February 24th, 1899.

Prof. PERRY, F.R.S., Vice-President, in the Chair.

A PAPER by Mr. E. F. J. LOVE, on "*The Joule-Thomson Effect and its Connection with the Characteristic Equation, and some of its Thermo-dynamical Consequences*," was read by Mr. WATSON.

The author points out that the results of the original Joule-Thomson investigation of the thermal effects of fluids in motion have been utilised hitherto almost exclusively for the one purpose of determining the relation between various gas-thermometer scales and the absolute scale of temperature. He proceeds to deduce further consequences from those results, indicating the relation between the formula assigned to the Joule-Thomson effect, regarded as a function of temperature, and the particular form adopted for the characteristic equation of a gas. He further attempts to supply a theoretical basis to the various formulæ of van der Waals, Rose-Innes, and others, at the same insisting upon a very high degree of accuracy for the original experimental work of Joule and Thomson. Then follows a discussion of the relation between the intrinsic energy of a gas and its volume, and a method is given for calculating the ratio of the principal two specific heats of a gas. Lastly, the author considers some points in the thermo-dynamics of substances at their temperature of maximum density. It is shown that (1) the Joule-Thomson effect for every substance at maximum density is zero; just as it is, though for a different reason, in the case of an ideal perfect gas. And (2) that the infinite number of specific heats possessed by every substance are, at the temperature corresponding to maximum density, reduced to one specific heat.

Mr. ROSE-INNES congratulated the author on having written an interesting paper on a difficult subject. At the same time he felt bound to acknowledge that he was out of sympathy with the general idea contained in the paper

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The experimental difficulties that occurred in carrying out the Joule-Thomson investigation were so enormous that it was better to rely on them as little as possible, notwithstanding the great skill of the experimenters. The Joule-Thomson results could not be disregarded altogether, since they were necessary for the establishment of the thermo-dynamic scale; but once that scale had been set up, it was better to have recourse as much as possible to such experiments as those of M. Amagat on the compressibility of gases. He also pointed out that one of the deductions given in the paper from van der Waals's formula had already been given by van der Waals himself.

Mr. WATSON replied, and the VICE-PRESIDENT proposed a vote of thanks to the author for his valuable paper. The meeting then adjourned until March 10th.

NOTICES OF BOOKS.

Practical Organic Chemistry for the Elementary and Advanced Examinations of the Science and Art Department. By GEORGE GEORGE, F.C.S. London: W. B. Clive, Correspondence College Press. Pp. 96.

As its name indicates, this book is intended for the use of Students preparing for the examination in Practical Organic Chemistry (Subject XI.) at the Science and Art Department. The author suggests that the student should first perform all the tests given for each substance, and then make up mixtures for himself and endeavour to detect the various ingredients: this would, of course, give him a certain amount of practice, but testing mixtures made by some one else will do far more real good; there is always a tendency to strain a point when you *know* what is present, and unfortunately the average student does not always sufficiently realise that his objective is to learn, and to acquire skill, not to merely solve puzzles and pass examinations.

The book is divided into eight chapters, in which the ordinary organic compounds—such as oxalic, tartaric, benzoic, acetic, carbolic, &c., acids; methyl and ethyl alcohols. sugars, glycerin, urea, &c.—are dealt with, and tests for recognising each given. In the last chapter the preparation of some of the reagents used in organic analysis is given.

The book is handy in size and clearly written, and should be found useful by those for whom it is intended.

A Text-book of Botany. By J. M. LOWSON, M.A., B.Sc., F.L.S. London: W. B. Clive, University Correspondence College Press. Pp. 394.

THE intention of the author in preparing this book was to provide a work that will be an efficient introduction to the subject, and include as well all the types set for the London University Intermediate Science and Preliminary Scientific Examinations.

The first part of the work is devoted to the general facts of structure and physiology; Part II. deals with the angiosperm, its seed, stem, root, leaf, nutrition, fruit, &c.; Part III. is on vascular cryptogams and flowering plants; and Part IV. on the lower cryptogams, such as liverworts and mosses, algæ, and fungi. There is a set of questions at the end of each part.

Royal Institution.—The Friday Evening Discourse on March 17th is on "The Electric Fish of the Nile," by Professor Francis Gotch; and that on March 24th on "Transparency and Opacity," by Lord Rayleigh.

CHEMICAL NOTICES FROM FOREIGN SOURCES

NOTE.—All degrees of temperature are Centigrade unless otherwise expressed.

Comptes Rendus Hebdomadaires des Séances, de l'Académie des Sciences. Vol. cxxviii., No. 5, January 30, 1899.

Explosibility of Acetylene at Low Temperatures.—Georges Claude.—The author shows that the solubility of acetylene in acetone increases with great rapidity as the temperature diminishes. At −80°, the temperature at which acetylene freezes, and under atmospheric pressure, acetone dissolves more than two thousand times its volume of gas. A platinum wire heated to redness by an electric current can be kept indefinitely in this solution without explosive decomposition occurring.

Alloys of Iron and Nickel.—F. Osmond.—The transformation points of alloys of iron and nickel have been determined for alloys containing less than 50 per cent of nickel. The author finds the same for alloys containing 50 to 100 per cent of nickel. It is not always easy to find the quantity of heat absorbed during the rise of temperature or given out during cooling. As this is so very small in many cases, the plan has been devised of determining the temperature at which magnetisation of the iron begins during the cooling and disappears during the heating process. The same method has been employed also to determine the transformation points of alloys containing under 50 per cent of nickel; the results being identical with those found by other methods. The author's results are given in a table and plotted on a curve.

Decomposition of Carbonic Oxide in presence of Metallic Oxides.—O. Boudouard.—The author extends his examination of decomposition of carbonic oxide by oxide of iron to oxides of nickel and cobalt. At a temperature of 455°, the same as that used in the former experiments, he finds that the carbonic oxide is totally decomposed by the oxides if the high temperature is maintained for a sufficient time. In the case of oxides of cobalt and nickel, the time necessary to arrive at the same results is shorter than in the case of iron.

A New Method of Estimating Carbonic Oxide.—MM. Schlagdenhauffen and Paget.—Oxides of silver and copper when heated in a current of carbonic oxide are completely reduced—the former at 60°, the latter at 300°—and can consequently be used to absorb the gas quantitatively. As the carbonic acid formed theoretically corresponds to the oxygen lost, it follows that the reaction may be used for the estimation of carbonic oxide.

Certain Iodine Compounds of the Aromatic Ketones.—A. Collet.—Only a small number of the iodine derivatives of the aromatic ketones is known—in particular, methyl-*p*-iodo-phenylketone. The author has obtained an iodo-methyl-phenyl ketone substituted in the methyl-group. The substance is prepared by treating chlorinated or brominated methyl-phenyl ketone in alcoholic solution with finely-powdered potassium iodide at the ordinary temperature. Chloride or bromide of potassium is formed, and the liquid, poured into excess of cold water, yields a crystalline mass, which possesses the composition $C_6H_5COCH_2I$. This body crystallises in colourless needles, which melt at 29°. Analogous substances were prepared in a similar manner, viz., iodo-methyl-*p*-tolyl ketone and iodo-ethyl-*p*-tolyl ketone. The vapours of these ketones exert an irritating effect upon the eyes. They are decomposable by light; their solutions in benzene or carbon bisulphine exposed to direct sunlight, turn rapidly violet, owing to liberation of a small quantity of iodine.

Preparation of Oxyethylamines.—F. Chancel.—Wurtz obtained oxyethylamines by the action of ammonia

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on ethylene oxide, and also by reacting with ammonia on glycol chlorhydrin. M. Chancel was able by this method to prepare the hydrochloride of trioxyethylamine not obtained by Wurtz; also the chloro-aurate of this base, the chloroplatinates of mono- and di-oxyethylamine, and the neutral oxylate of mono-oxyethylamine.

Extraction and Synthesis of the Perfume Principle of the Flower of Jasmine.—Albert Verley.—For several years attempts have been made to extract the essential oil of the jasmine flower. This cannot be distilled with steam, since it only exists in the plant in small quantity, and is completely destroyed by prolonged boiling with slightly acidulated water. The author has succeeded in obtaining the perfume in the following manner:—The fresh jasmine flowers, picked in the morning dew, were enclosed in glass cases greased on the interior. The grease absorbed the perfume exhaled by the flowers, the faded ones being replaced by fresh each morning. After some days, the grease was washed with oil of vaseline, which removed the essence. The oil of vaseline was then extracted with acetone, and the latter evaporated *in vacuo*. The residue consisted of an oil, of a clear red colour, which possessed the characteristic odour of jasmine in a greatly intensified degree. This was fractionated under a pressure of 12 m.m. Analysis ascribed the formula $C_9H_{10}O_2$. The body possessed the properties of neither an aldehyde nor a ketone. Oxidation proved the presence of a benzene nucleus in its molecule, and it was finally classed as an acetal. Synthesis of the perfume was effected from phenylglycol and formaldehyde in presence of water and sulphuric acid.

Action of Di-diazochlorides of Benzidine, Orthotoluidine, and Orthodianisidine on Acetylacetone.—G. Favrel.—Not suitable for abstraction.

No. 6, February 6, 1899.

Oxidation of certain Ureas.—Œschner de Coninck.—The ureas were treated with a mixture of neutral potassium chromate and sulphuric acid. In the case of urea, the resulting gas was chiefly CO_2 and a small quantity of nitrogen; sulpho-urea gave sulphocyanic acid as its principal decomposition product, also a residue of ammonium sulphate,—

$$CS<^{NH_2}_{NH_2}+4O+2H_2O=CO_2+(NH_4)_2SO_4.$$

Phenyl-sulphourea, diphenylsulphourea, methylurea, phenylurea, and diphenylurea gave in each case pure CO_2. Benzylurea gave CO_2 and, amongst other products, a small quantity of benzylcarbimide,—

$$CO<^{NH.C_6H_5.CH_2}_{NH_2}=NH_3+CO.N.C_6H_5CH_2.$$

Researches on the Latent Heat of Vaporisation of Piperidine, Pyridine, Acetonitrile, and Capronitrile.—W. Longuinine.—Not suitable for abstraction.

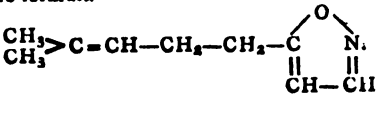
Methyloctenonal.—G. Leser.—The study of the derivatives of this body shows that in certain reactions it has functions under its normal form—

$$\begin{matrix}CH_3\\CH_3\end{matrix}>C=CH-CH_2-CH_2-CO-CH_2-GHO;$$

but in other cases it possesses the tautomeric oxymethylene constitution,—

$$\begin{matrix}CH_3\\CH_3\end{matrix}>C=CH-CH_2-CH_2-CO-CH=CHOH.$$

Treated with hydroxylamine, an isoxazol was obtained, having the formula—



This is changed into the isomeric nitrile,—

$$\begin{matrix}CH_3\\CH_3\end{matrix}>C=CH-CH_2-CH_2-CO-CH_2-CN,$$

by treating in the cold with sodium ethylate, and afterwards adding the calculated quantity of acetic acid. Aniline and methylaniline react with methyloctenonal to give anilides.

Bulletin de la Société Chimique de Paris.
Series 3, Vol. xix.-xx., No. 12.

The Limits of Inflammability of Gaseous Mixtures.—H. Le Chatelier and O. Boudouard.—Already inserted.

The Mixed Halogen Salts of Lead.—V. Thomas.—Already inserted in full.

General Reaction of Ethenic Carbides. Corresponding Mercuric Compounds.—Already inserted.

Action of Bromine on Bromide of Ethyl in the presence of Bromide of Aluminium. Preparation of Bromide of Ethylene, (CH_2Br-CH_2Br).—A. Mouneyrat.—Already inserted.

Action of Chloride of Aluminium on Tetrachloride of Acetylene.—A. Mouneyrat.—When these two bodies are heated together to 110° on a paraffin bath a regular disengagement of hydrochloric acid takes place, and the mass becomes darker; when a quantity of hydrochloric acid corresponding to $CCl\equiv CCl$ has been collected in the wash bottles, the contents of the flask are thrown into iced water containing a little HCl, the oil after washing and drying is distilled fractionally and two liquids are obtained, one passing over between 130—135° and the other at 147°; the first part is $C_2H_2Cl_4$, and the other is unchanged symmetric tetrachlorethane, $CHCl_2-CHCl_2$.

Action of Bromine on Tetrachloride of Acetylene in the presence of Chloride of Aluminium.—A. Mouneyrat.—188 grms. of tetrachloride of acetylene, 320 grms. of bromine, and 25 grms. of powdered chloride of aluminium, all perfectly dry, are heated in a flask, fitted with a vertical condenser, to 105°, on a paraffin bath, until all the bromine has disappeared; the heavy dark coloured liquid remaining is thrown into distilled water containing a little HCl; after drying it is distilled *in vacuo*, and the greater part of the liquid boils at 140° at a pressure of 7 c.m., and at 194—195° under 76 c.m.: this body has the formula $C_2H_2Cl_2Br_2$, and is therefore dibromodichlorethane.

The Biochemical Preparation of Dioxyacetone (Propanediolone).—G. Bertrand.—Not suitable for abstraction.

Pyrocatechin-ethane and its Derivatives.—Ch. Moureu.—Already inserted.

Heat of Formation of some Quinones with a High Molecular Weight. Thermo-chemistry.—A. Valeur.—Already inserted.

The Quionoximes.—A. Valeur.—Already inserted.

Some Amido-amidines (IV.).—F. Muttelet.—When equal parts of dinitraniline and chloride of benzoyl are heated together on an oil bath, at about 140—150°, a violent effervescence is observed, which continues until fusion is complete, when the temperature will reach 170—180°; the brown product is washed with benzene; the yellow powder thus obtained is only slightly soluble in the ordinary solvents; it is obtained in yellow crystalline grains, melting at 220° with the help of boiling toluene. Analysis shows it to have the formula of a benzoyl derivative, $(NO_2)_2.C_6H_3.NH.CO.C_6H_5$.

On the Ketones having the Odour of Violets, and on the Compounds of the Citral Series (Geraniol), to which they are Allied.—F. Tiemann.—A very long paper, not suitable for abstraction.

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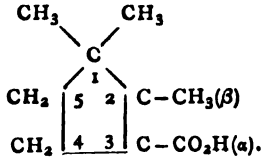
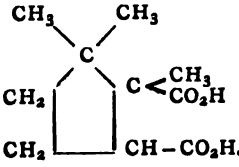
Action of Chlorids of *m*-Nitrated Benzoyl on the Mono-substituted Orthodiamines.—F. Muttelet.—Not suitable for abstraction.

The Constitution of Isolauronolic and Camphoric Acids.—G. Blanc.—The author concludes that the constitution of isolauronolic acid is now fixed with the utmost certainty, and it is dimethyl-1.1 methyl-2-cyclopentene-Δ_2-methyloïc-3 acid.



Camphoric acid is represented thus:—



Absinthine. — P. Bourcet. — Absinthine is a white inodorous body, of extreme and persistent bitterness, crystallising in very fine prismatic needles. It melts at 68°, but traces of impurities lower its melting-point to 65—66°. Absinthine is a glucoside which does not contain any nitrogen; its formula is $C_{15}H_{20}O_4$.

Method of Estimating the Perchlorate in Nitrates of Soda and of Potash.—N. Blattner and J. Brasseur.—Already inserted in full.

Journal de Pharmacie et de Chimie, Series 6, Vol. viii., No. 6.

Volumetric Estimation of the Nitrogen in Urea, or of Urea, by means of an Alkaline Solution of Hypobromite of Soda. — H. Moreigne. — The author describes two methods for this estimation:—1st, after treating the urine with phosphotungstic acid; and 2nd, after treatment with basic acetate of lead and phosphotungstic acid. At first sight the phosphotungstic acid method would appear to be very delicate and require great skill; it is, however, as simple as the well-known basic acetate of lead process, and has this advantage, that it is more accurate. In the second method described the author's idea was to associate the eliminating action of the basic acetate of lead with that of the phosphotungstic reagent. This process, though as simple as the former one from the manipulating point of view, is, however, a little longer, as it requires two precipitations and two filtrations.

Estimation of Sugar in Chocolate. — P. Carles.—16·20 grms. of powdered chocolate are placed in a 100 c.c. flask with about 80 c.c. of water, and boiled on the water-bath for half an hour; 2 or 3 c.c. of a solution of subacetate of lead are then added, the contents are well shaken, and made up to 100 c.c. Cool and filter. The colourless liquor is examined in the saccharimeter, and the reading N found is modified by the following formula, which gives the result sought for:—

$$N - \frac{N \times 8{\cdot}10}{100} = x.$$

On a Chloro-iodide of Tin.—C. Lenormand.—Already inserted in full.

Vol. viii., Nos. 7 and 8.

These two numbers contain no matter of chemical interest.

Vol. viii., No. 9.

The Volumetric Estimation of Ethylic Aldehyde. —M. Rocques.—In devising a new method for the estimation of ethylic aldehyde the author has made use of three quantitative reactions of aldehyde:—1. The action of sulphurous acid on bisulphites; 2. The action of nitrate of silver in the presence of ammonia and caustic soda; and 3. The action of hypochlorites. The first method gave the best and most concordant result. The method of working was as follows:—Two solutions, S and I, were prepared, the first by dissolving 12 6 grms. of pure sulphite of soda in 400 c.c. of water, adding 100 c.c. of sulphuric acid, and making the volume up to 1 litre with pure alcohol at 96°. This is filtered on the following day. The second solution is a normal solution of iodine in iodide of potassium; 1 c.c. corresponds to 0·0032 grm. of sulphurous acid and to 0·0022 grm. of ethylic aldehyde. The solution S is titrated by means of the solution I in the presence of starch; 10 c.c. of S should require 20 c.c. of I. To estimate the aldehyde in an alcoholic solution we place 10 c.c. in a 100 c.c. flask, add 50 c.c. of S, and make up to 100 c.c. with pure alcohol at 50°; in another flask we put 50 c.c. of S, and make up to 100 c.c. with pure alcohol at 50°; both flasks must be well shaken. On the following day take 50 c.c. of each and titrate the free sulphurous acid with solution I, adding about 50 c.c. of water and a little starch. If A is the number of cubic centimetres of solution I required by the check solution, and *a* the number required by the solution containing the aldehyde, the proportion of aldehyde present per litre will be $(A-a) \times 0{\cdot}0022 \times 200$. If the solution contains less than 1 per cent of aldehyde the solutions S and I must be diluted.

Vol. viii., No. 10.

This number contains no matter of chemical interest.

Vol. viii., No. 11.

Digitalic Ferment.—MM. Brissemoret and Joanne.—In 1875 Kosmann prepared a nitrated substance from the leaves of purple digitalis, which he regarded as a hydrating ferment. According to him this ferment had the properties of diastase; it transforms, by hydration, cane-sugar into glucose, starch into dextrine, and salicine into glucose and saligenine. The authors find that it possesses oxidising properties, has great analogies with the oxidases isolated by Bertrand from a large number of vegetable phanerogams, and is not destroyed by desiccation.

The Volumetric Estimation of Ethylic Alcohol.—X. Rocques.—Further experiments on the estimation of ethylic alcohol by the action of alkaline bisulphites on this body show that temperature exercises a considerable influence on the reaction, and, while the reaction is complete in less than twenty-four hours at 25° to 30°, it is not finished after forty-eight hours when the temperature is lowered to 15°.

MISCELLANEOUS.

Royal Institution.—A General Monthly Meeting of the Members of the Royal Institution was held on the 6th inst., Sir James Crichton-Browne, M.D., F.R.S., Treasurer and Vice-President, presiding. The following were elected Members:—W. B. Bannerman, A. Bellin, Lady Currie, C. H. Gatty, A. C. Gibbons, E. J. Gibbons, Mrs. Horne, Mrs. Kraftmeier, Sir G. H. Lewis, Mrs. J. List, F. J. Longton, O. S. Macleay, Mrs. Parker, H. Pulford, and Colonel E. Sartorius, V.C., C.B. The special thanks of the Members were returned to Sir Andrew Noble, K.C.B., for his donation of £100, and to Mr. Edward Kraftmeier for his donation of £52 10s. to the fund for the promotion of Experimental Research at Low Temperatures. His Grace the Duke of Northumberland

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was elected President of the Royal Institution in the place of the late Duke, his father.

Water Supplies and the Fever Death-rate.—In a letter to a provincial contemporary, Mr. A. H. Smee gives some very interesting figures bearing on the fever death-rate and the water supplies of various large towns, both in Great Britain and on the Continent. Out of twenty-two towns in Great Britain it is very satisfactory to note that London, the *only one* supplied with river water, is almost the best, the fever death-rate being only 67 per million; Brighton 66, Bristol 56, and Plymouth 40, being the only towns to beat it, whereas the much vaunted supplies of Glasgow, Liverpool, and Manchester give fever death-rates of 184, 172, and 133 respectively. Belfast is the worst, with 1667 per million.

A Table for the Restoration of Weak Sulphuric Acid to Acid of 98 per cent H_2SO_4.—This useful table, calculated and checked by Messrs. R. Friswell, F.I.C., T. Lawson, F.I.C., and F. Evershed, F.C.S., and published by Messrs. Brooke, Simpson, and Spiller, Ltd., shows at a glance the number of lbs. of "oleum" containing 60 per cent SO_3 and 40 per cent H_2SO_4 to be added to 1000 lbs. of weak acid of specific gravities varying from 1·7 to 1·8 in order to bring it up to the strength 98 per cent H_2SO_4. The table is available for pure dilute sulphuric acid by a determination of the specific gravity, and in other cases by a determination of the sulphuric acid, calculated either as SO_3 or H_2SO_4.

MEETINGS FOR THE WEEK.

MONDAY, 13th.—Society of Arts, 8 (Cantor Lectures). "Cycle Construction and Design," by Archibald Sharpe, A.M.Inst.C.E.

TUESDAY, 14th.—Royal Institution, 3. "The Morphology of the Mollusca," by Prof. E. Ray Lankester, M.A., LL.D.

WEDNESDAY, 15th.—Society of Arts, 8. "Liquid Fuel," by Sir Marcus Samuel.

— Microscopical, 8. "The Projection Microscope." by Lewis Wright.

— Institution of Mining and Metallurgy, 8. "On Crushing and Concentration at Dolcoath Mine, Cornwall," by R. Arthur Thomas, M.Inst.M.M. "On Charcoal Precipitation from Auro-Cyanide Solutions," by John I. Lowles, M.Inst.M.M. "Notes on the Electro-Deposition of Vanadium," by Sherard Cowper-Coles, M.Inst.M.M.

THURSDAY, 16th.—Royal Institution, 3. "English Playhouses in the Sixteenth, Seventeenth, and Eighteenth Centuries," by William Poel.

— Chemical, 8. "Influence of Substitution on Specific Rotation on the Bornylamine Series," by H. O. Forster, Ph.D. "Rotatory Power of Optically Active Methoxy- and Ethoxy-Propionic Acids prepared from Active Lactic Acid," by Thomas Purdie, F.R.S., and James C. Irvine, B.Sc.

FRIDAY, 10th.—Royal Institution, 9. "The Electric Fish of the Nile," by Prof. Francis Gotch, F.R.S.

SATURDAY, 18th.—Royal Institution, 3. "The Mechanical Properties of Bodies," by The Right Hon. Lord Rayleigh, F.R.S., &c.

TECHNOLOGICAL EXAMINATIONS, 1899.
CITY AND GUILDS OF LONDON INSTITUTE.

The Institute's Examinations in Technology will be held on April 26th, 29th, May 1st, 2nd, 3rd, 4th, 6th, 8th, 9th, 12th, 13th, June 3rd and 10th.

All applications from Local Secretaries for examination in Technology must be forwarded to the Institute on or before March 20th.

Only in exceptional cases, and by payment of an additional fee, can applications be received from Local Secretaries after that date.

Candidates in Technology not attending any registered class should apply at once to the Secretary of the nearest Local Centre.

Applications from any individual candidates for examination at the Offices of the Institute should be made not later than March 30th, addressed to the Examinations Department, City and Guilds of London Institute, Exhibition Road, London, S.W., and should be accompanied by a Postal Order for the amount of the fee—the Subject and Grade of Examination being clearly stated.

By Order of the Directors, who are transferring their business to their other Works.

TO CHEMICAL AND MANURE MANUFACTURERS, ENGINEERS, MACHINERY USERS, AND OTHERS.

VICTORIA DOCKS.—Sale of the remaining Plant and Machinery, situate at Messrs James Gibbs and Co.'s, Upper Works, North Woolwich Road.

MESSRS. GREEN and SON are instructed by the Directors to SELL by AUCTION, in Lots, on the Premises, Upper Works, North Woolwich Road, on MONDAY, MARCH 20, 1899, at Twelve for One o'clock precisely, the remaining CHEMICAL PLANT, Machinery, and other matters belonging to Messrs. James Gibbs and Co. (Limited), and comprising manure plant, alum cake plant, including wrought iron calcining cylinder, 54 ft. long, with furnace; phosphate mill plant, including eight pairs of 4 ft. 6 in. mill stones, complete with gear, Blake Marsden stone crusher, four Mumford and Moodie's separators; the acid plant, comprising two sets of pyrites kilns, with 56 furnace fronts, fitted complete, with doors, bars, &c., acid eggs, &c.; the steam power includes a splendid 200 h.p. steam engine, with high and low pressure cylinders and eight C.I surface condensers by Simpson and Co., a double cylinder tandem air compressor, and two small engines, six Cornish boilers, 6 ft. dia. by 28 ft. long, about 500 ft. of shafting, with pulleys, riggers, and belting; two three-ton cranes, four-ton weighbridge, and two three-ton ditto; about 1000 ft. of tram lines, and about 300 iron columns each 18 ft. to 20 ft long, forge, sundry utensils, tools, two useful vans, office furniture, &c.

NOTE. The Freehold Property, covering an area of over three acres, with frontage of 100 ft. to the river, and comprising useful buildings, is for sale by private contract.

May be viewed on the Friday and Saturday prior to the Sale.

Catalogues of Messrs. LINKLATER, ADDISON, BROWN, and JONES, Solicitors, 2, Bond Court, Walbrook, E.C.; on the Premises; and of Messrs. GREEN and SON, Auctioneers and Surveyors, 28 and 29, St. Swithin's Lane, E.C.

TO MANUFACTURERS AND OTHERS REQUIRING STEAM POWER.

By Order of the Directors of JAMES GIBBS and CO. (Limited).—Sale of Remaining Plant and Machinery at VICTORIA DOCK,

MESSRS. GREEN and SON desire to draw particular attention of purchasers of machinery to Lot 118 at their Sale on Monday, March 20, as noticed above. It comprises a splendid 200 h.p. COMPOUND CONDENSING STEAM ENGINE by Simpsons, of Pimlico. It has been in working order for several years, and shows particularly satisfactory working; it is most compact and in thorough order, the whole being well set and standing on brick and stone foundations. The average pressure of 60 lb. and 45 revolutions gives the indicated h.p. as mentioned above, and, with slightly increased pressure, can easily work to 300 h.p.

Catalogues of Messrs. GREEN and SON, Auctioneers and Surveyors, 28 and 29, St. Swithin's Lane, E.C,

TO MANUFACTURING AND BUSINESS FIRMS.

TO BE SOLD.
FREEHOLD LONDON PROPERTIES,

offering good opportunities for a large firm requiring a branch establishment in London.

I.—Freehold property, area three acres, frontage of 190 feet to the River Thames. Good depth of water, and covered with buildings suitable for many purposes.

II.—Freehold Property, within 2¼ miles of the City. Waterside frontage of 290 feet, and some very substantial buildings, with room for extension.

III.—Compact Manufacturing Premises. Waterside frontage of 154 feet, area 31,000 square feet, substantial buildings, and fitted with steam power.

Particulars of the above may be obtained from Messrs. GREEN and SON, Auctioneers and Surveyors, 28 and 29, St. Swithin's Lane, London, E.C.

THE YORKSHIRE COLLEGE, LEEDS.

DEPARTMENT OF LEATHER INDUSTRIES.

Applications will be received up to March 16th for the Appointment of ASSISTANT LECTURER and DEMONSTRATOR in LEATHER INDUSTRIES. A sound training in Chemistry is essential; Technical Knowledge, although desirable, is not indispensable. Salary to commence at £150 a year.—Further particulars may be obtained from the SECRETARY of the College.

FOR SALE.—Chemical Balance by Oertling. Perfect condition, good as new, cost 18 guineas.—For particulars apply to "Analyst," care of Mr. Wilson, Chemist, Ordnance Road, Enfield Lock, London, N.

LABORATORY TO BE LET.—Centrally situated. Very moderate rental.—Address, "Laboratory," care of Housekeeper, 34, Old Broad Street, E.C.

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THE CHEMICAL NEWS.

Vol. LXXIX., No. 2051.

ON HYDROGEN PEROXIDE AS THE ACTIVE AGENT IN PRODUCING PICTURES ON A PHOTOGRAPHIC PLATE IN THE DARK.*

By W. J. RUSSELL, Ph.D., V.P.R.S.

In previous papers it has been shown that certain bodies are able, in the dark, to act on a photographic plate and produce a picture. The purpose of the present communication is to show that in all the cases which have been examined, and probably in all others of a similar kind, the action which occurs is due to the presence of hydrogen peroxide. As a sensitive plate always contains moisture, and probably would be inactive if quite dry, it does not seem possible to test the truth of this statement by the total exclusion of moisture; therefore more indirect means have to be adopted. In the following paper no attempt is made to explain the reactions which occur in the plate itself; that is a distinct question, and at present the object is to consider the means by which these changes, whatever they may be, are brought about. These changes are rendered visible by exactly the same processes as those adopted for the development of an ordinary light picture. Any of the ordinary photographic plates may be used in these experiments, but as many of the pictures are only formed after a long exposure it is well to use rapid plates. In the following experiments the plate used has been in almost all cases the "Ilford special rapid," and the process of development has in every case been that recommended for their ordinary use.

The first step towards demonstrating that hydrogen peroxide is the active agent in producing these pictures, is to show that all the results produced both by metals and by organic bodies on a photographic plate can be produced by hydrogen peroxide. This body is now made in considerable quantities and sold in aqueous solution of a given strength. This commercial article appears to act equally well to a carefully prepared and pure specimen of the same strength.

A convenient way of testing the action of any liquid on a photographic plate is to use a small circular glass dish, such as is made for bacteriological experiments, the photographic plate resting on the top of the dish, and the amount of the liquid used determines the distance the plate is from the active surface, the experiment being carried on in complete darkness. If pure water be tested in this way, it is found that no picture, that is no darkening of the plate, occurs on its being treated with the developing solution. The plate can be left over the water for eighteen to twenty hours, but if left longer than this the film is destroyed by the aqueous vapour. If to the pure water in the dish a mere trace of hydrogen peroxide be added, a darkening of the plate will quickly occur. For instance, if the liquid contains only one part of the peroxide in a million of water, and the plate be exposed to its action for eighteen hours, a faint picture is produced. Bearing in mind the small amount of evaporation which takes place under these conditions, and consequently the minute amount of the peroxide which comes in contact with the plate, it clearly shows the exceeding delicacy of the reaction.

Again, if a piece of Ford blotting-paper, which by itself is inactive, be wetted with a solution of one part of peroxide in 500,000 of water, and be hung up in a warm room for three-quarters of an hour to dry, and placed in contact with a photographic plate for two hours at a temperature of 55° C., on subjecting the plate to development a distinct picture is produced. In fact, moistening good blotting-paper with a solution which may be strong or weak, and allowing it to dry, for a short time, is a very good way of applying the peroxide. In place of blotting-paper any inactive porous substance may be used.

Plaster of Paris wetted with a peroxide solution and allowed to set, continues for a long time to be an active body. If by any of these means a large, in place of a small, amount of the peroxide be allowed to act on a plate, then in place of a dark, a light picture is obtained, a phenomenon similar to what is known to photographers as reversal.

The conditions under which certain metals and certain organic bodies act on photographic plates, and how pictures of the structure of paper, skeleton leaves, lace, and other bodies can be obtained, has already been described, so that now it is only necessary to say that substitute for these active bodies peroxide of hydrogen, and exactly corresponding results are produced. Writing with ordinary ink, or with a solution of ferrous sulphate, or potassium ferrocyanide, has been shown to be opaque to the action of zinc and of turpentine, so is it to the action of the peroxide of hydrogen. Further, the action exerted by the metals and the terpenes is unable to pass through glass, mica, selenite, &c., but is able to pass through thin sheets of gelatin, celluloid, guttapercha, indiarubber, tracing-paper, gold-beaters' skin, parchment, &c.; peroxide of hydrogen acts exactly in the same way, every body which is known to be either opaque or transparent to the action of the metals or terpenes is opaque or transpareni to the action of the peroxide; so that, as far as the production of similar phenomena goes, the agreement is complete. Of the acknowledged tests for the preeence of hydrogen peroxide, the one with the titanic acid dissolved in sulphuric acid is exceedingly delicate; so also appears to be the tetramethylparaphenylenediamine paper of Dr. Wurster, and both of them have been made use of.

The next point which naturally suggests itself is, whether peroxide of hydrogen is, or is likely to be, present in all the different cases, when action on the sensitive plate occurs. First, with regard to the metals. The list of the active metals, which has already been given, is as follows, arranged approximately in order of their activity:—Magnesium, cadmium, zinc, nickel, aluminium, lead, cobalt, bismuth, tin. Now these are certainly the metals which might be expected to decompose water, and in the presence of oxygen cause the formation of hydrogen peroxide, and still more the order in which they stand in the above list, judging from their general properties, is that in which they would probably induce the formation of the peroxide. It is also satisfactory to note that this list of metals and their order of activity was drawn up simply from experiment, when there was no idea that hydrogen peroxide had anything to do with the reaction. Again, as a confirmation that hydrogen peroxide is formed when these metals oxidise in moist air, pieces of Dr. Wurster's tetra-paper were moistened and laid on bright surfaces of the metal. With the metals that head the foregoing list a considerable amount of blue colour was rapidly developed; with the metals at the end of the list the amount of colour was less, and the reaction slower; and with other metals, such as silver and platinum, there was no action. With copper and with iron a very slight amount of action did occur, but these metals do not appear able to produce definite pictures. Iodide of potassium and starch paper, where used in the same way, gave a blue colour with all the active metals, but none with copper nor with iron.

On the supposition that hydrogen peroxide is the active agent in the action exerted by the metals, it seemed probable that on supplying to the metal more moisture than it obtained from the air and photographic plate, more action would take place, and this was found to be the case. Two pieces of polished zinc were placed in contact with photographic plates in small iron boxes; one box was

* A Paper read before the Royal Society, March 2, 1899.

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quite dry, and put in a bell jar over calcium chloride, and into the other box some damp paper was introduced, and the box was placed with a little water under a bell jar. On examining the plates after three days it was found that the damp plate had much the darker picture on it.

With the object of obtaining an increased amount of action, experiments were made by passing a current of warm moist air over zinc turnings. A glass tube, 6 feet long and 1 inch in diameter, was packed with zinc turnings and placed within a large brass tube to which steam could be admitted. The amount of action, if any, was indicated on a plate, placed in a dark box at the end of the tube. Even under the most favourable conditions no very large amount of action took place. When a current of moist warm air was passed through the tube for an hour a fairly dark picture was obtained. If the air was dry no picture appeared. If amalgamated zinc was used in place of pure zinc a darker picture was formed, and, as a check on these results, dry and moist air, both warm and at ordinary temperatures, was passed through the tube, no zinc being present, and then no action took place. Also when ozonised air was passed through the tube there was no action. Passing now from the metals to the organic bodies capable of acting on a photographic plate, it has been found that they belong essentially, if not solely, to that class of bodies known as terpenes, and it is a general property of all this class of bodies when oxidising to give rise to hydrogen peroxide. Thanks to Dr. Tilden, experiments have been made with most of the terpenes, and all were found to be very active bodies; both pinene and limonene were tried, in their dextro- and lævo-rotatory state, but their activity appeared to be the same. Oxidised and other compounds connected with the terpenes, such as terpineol camphor, thymol cymene, have no power of acting on a photographic plate, but ordinary turpentine and terebene are very active bodies.

Most of the ordinary essential oils, such as bergamot, peppermint, pine, lemons, cajuput, &c., have been experimented with, and, without exception, have been found to be active bodies. It is well known that they all contain terpenes; they are also characterised by a strong odour, and as ordinary scents contain some of these bodies, it follows that almost all vegetable bodies having a strong smell are capable of acting on a photographic plate. Eau de Cologne gives a good picture, so do many wines and brandy, and coffee, guiacum, cinnamon are also active substances; thus the photographic plate becomes a very delicate test for the presence of all these bodies, and as the action is cumulative it may even compete with the sense of smell.

In addition to the essential oils, the ordinary vegetable oils, such as linseed oil, which is the most active, and colza and olive, which are much less active and have much less power of absorbing oxygen from the air, can act on a photographic plate. The tetra-paper readily goes blue if suspended in a bell jar which has a few drops of linseed oil in a dish within it.

The mineral oils are, on the contrary, devoid of this power of acting on the sensitive plate, and the same applies to bodies such as benzene, phenol, naphthalene, aldehyde, methyl alcohol, coal naphtha, &c.

It would seem, then, that all the organic bodies capable of acting on the photographic plate are capable of giving rise to the formation of hydrogen peroxide when they oxidise in moist air.

(To be continued).

On 2-Oxydibenzalacetone.—St. v. Kostanecki and D. Maron.—The results are here given which were obtained with some colouring-matters containing chromophore, C=C.CO.C=C, a compound with the same members arranged in a different order. These compounds take rise from the action of aldehyds on an unsaturated ketone, $R.CH=CH.CO.CH_3$, prepared from acetone. Among the aldehyds, benzaldehyd, furfurol, and piperonal have been used.—*Ber. Deutsch. Chem. Gesell.*

A CONTRIBUTION TO AGRICULTURAL CHEMISTRY: CARDAMOMS.

By H. B. YARDLEY.

Having made search in likely publications, I can find no analyses of the ash of *Cardamoms*, either plant or seed; it may therefore be interesting to others and desirable to place on record the annexed analysis of some of the seeds (and husks) performed in my laboratory lately:—

The mineral matters (ash) amounted to 4·19 per cent. It was of a grey colour, probably due to a small quantity of carbon which it was found impossible to entirely burn off. This ash gave:—

Lime	13·33
Oxide of iron	0·51
Alumina	1·53
Magnesia	4·52
Soda	20·43
Potash	10·42
Phosphoric anhydride	6·00*
Sulphuric anhydride	12 66
Chlorine	2·54
Silica	24·81
Carbonic anhydride, carbon, &c.	4·40
	101·15
Less oxygen = chlorine	1·15
	100·00

* Equal to tribasic phosphate of lime.

The organic constitution of the seeds was not required, and there are already published records.

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London, N.E.

THE SEPARATION AND ESTIMATION OF LEAD BY ELECTRICAL MEANS IN ITS PRINCIPAL ALLOYS AND IN COMMERCIAL METALS.

By A. HOLLARD.

The estimation of lead by electrical means in the state of binoxide is of incomparable exactness and simplicity, provided that a certain number of precautions are observed very closely, such as density of current, composition of the electrolyte, temperature of desiccation of the deposit of binoxide of lead, &c. These data have up to the present been incomplete, and the results sometimes incorrect; we believe we have now elaborated and defined them in a strict manner. We have also laid down the conditions under which the method may be applied to the most widely divergent alloys. It is only after experiments carried out under the most varying conditions and methods of control, during the course of several years, that we publish this method, believing that it will be found to be of great service.

The deposits of binoxide of lead which occur exclusively on the anode are *very adherent*, and correspond exactly to the formula PbO_2; further, no trace of metallic lead is deposited on the cathode.

The quantity of lead submitted to estimation need not be more than 0·2 grm.; with a larger quantity, in fact, there is a danger of the deposit not being sufficiently adherent.

Electrolytic Apparatus.—Our electrodes consist of a truncated cone of platinum which serves as anode, and on which the binoxide of lead is deposited; the cathode is a spiral of platinum wire fixed on a stand. They are, in fact, Lukow's apparatus modified as to construction

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and dimensions; the truncated cone is made of a sheet of pure platinum, its upper diameter is 18 m.m. and its lower diameter 45 m.m., its generatrix 63 m.m. A hard platinum wire is gold-soldered to the trunk of the cone. Each electrode weighs about 20 grms.

The vessels containing the electrolytes are of ordinary cylindrical Bohemian glass, about 6·5 c.m. diameter, holding about 370 to 400 c.c. The solution of the alloy, as well as the electrolysis of the lead, is conducted in the same beaker; the whole operation does not require, as will be seen, either decantation or filtration. During the attack with acid the beaker must be covered with a funnel, the edge of which should rest just inside the edge of the beaker, forming a little gutter in which a few drops of water will make a perfect hydraulic joint; all loss by projection is thus avoided. The distance from the lower edge of the cone to the foot of the spiral should be about 6 m.m. For better receiving the electrolytic deposit of lead the cone should not be polished, but dull, so that the deposit will adhere to it more easily. This can be effected by immersing the platinum in aqua regia for a few hours.

I. *Estimation of Pure Lead.*

The lead is dissolved in dilute nitric acid. The solution, diluted to about 350 c.c., should contain 80 c.c. of ordinary pure nitric acid in the free state. With a less quantity of acid there is a liability to deposit part of the lead on the cathode. The electrolysis is effected at the ordinary temperature with a current of 0·15 ampère. The voltage cannot be defined; it depends on the quantity of lead in the electrolyte, and, in the case of alloys, on the nature and proportion of foreign metals present.*

The cone should be plunged completely into the bath, and the foot of the spiral should be as near as possible to the bottom of the beaker. The electrolysis goes on at the ordinary temperature. At the end of twenty-four hours the precipitation is complete and the deposit very adherent. The cone is then plunged successively into two beakers filled with distilled water, and then placed in in an oven and heated gradually to 200°, which temperature should be maintained for a quarter of an hour. *This temperature is absolutely necessary to obtain a deposit corresponding exactly with the formula* PbO_2.

II. *Separation and Estimation of Lead in Commercial Zinc.*

Ten or twenty grms. of zinc, according to the purity of the metal, are dissolved in such a quantity of dilute nitric acid that when the solution is effected, 80 c.c. of ordinary pure nitric acid remain in the free state (1 grm. of zinc in dissolving combines with 3·5 c.c. of ordinary pure acid. The rest of the operation is carried out as described above.

The lead once separated, the other impurities in the zinc can be estimated very easily, and much more easily than by the ordinary method. The estimation of cadmium in particular, so difficult by the ordinary method, becomes very simple; the whole of this metal is, in fact, found in the bath, free from lead; it suffices to evaporate down this solution, in presence of sulphuric acid, to drive off the nitric acid, and then precipitate the cadmium by means of sulphuretted hydrogen in the ordinary way.

III. *Separation and Estimation of Lead in Alloys of Lead and Tin, and in Commercial Tin.*

1. *An Alloy containing more than 4 per cent of Lead.*—Proceed as described above (Part I.), taking note in the determination of the amount of free acid present that 1 grm. of tin decomposes while dissolving 2 c.c. of ordinary pure nitric acid. The alloy should be in the form of fine turnings, or, better still, filings. The precipitated oxide of tin should not be filtered; it should simply be collected together at the bottom of the beaker in the following manner:—The solution, diluted to about 350 c.c., should be heated to 90° until the oxide of tin collects at the bottom; the flame is then taken away, when the deposit remains compact on cooling.

2. *Alloys containing less than 4 per cent of Lead.*—These alloys contain a large proportion of tin in comparison with the amount of lead present, and their solutions should be electrolysed in very large beakers. Under these conditions the oxide of tin forms a thin layer at the bottom of the beaker; there is then no risk of carrying off lead from the solution, or even of retaining small particles of unattacked alloy, and thus losing a part of the metal under analysis. The beakers, which will serve both for the solution of the alloy and electrolysis, should be 10·5 c.m. in diameter with a capacity of about 1 litre. The solution should be effected warm on 5 grms. of the alloy, with dilute nitric acid containing 260 c.c. of ordinary pure acid. The solution should then be diluted to about 650 c.c.; the oxide of tin is then collected at the bottom of the beaker as described above.

3. *Commercial Tin.*—This should be treated in exactly the same manner as alloys containing less than 4 per cent of lead (2).

IV. *Separation and Estimation of Lead in Alloys of Lead and Antimony, and in Commercial Antimony.*

As the deposits of binoxide of lead carry with them oxide of antimony, the method we have described for tin and its alloys is not applicable. This oxide of antimony comes from the antimony dissolved in the solution.

V. *Separation and Estimation of Lead in Commercial Copper and its Alloys (Brasses and Bronzes).*

In the presence of a certain amount of copper, the integral separation of lead in the state of binoxide requires a much smaller quantity of nitric acid and a stronger current than in the preceding cases. We shall give the reason for this later on.

We take a quantity of the alloy, or of copper containing at least 1 grm. of this metal, and we attack it with dilute nitric acid in sufficient quantity to leave an excess of 14 c.c. of ordinary pure nitric acid after solution; 1 grm. of copper in dissolving combines with 3·6 c.c. of this acid. The solution is diluted to 350 c.c. The intensity of the current should be 0·3 ampère, and the duration of the electrolysis about eighteen hours.

When lead is present in the copper or its alloys, as an impurity only, we take 10 grms. of the metal, as has already been pointed out in the analysis of the impurities of commercial copper (A. Hollard, *Comptes Rendus*, cxxiii., p. 1065), bronzes and brasses (A. Hollard, *Bull. Soc. Chim.*, 1897, Series 3, xvii., 886).

Reactions produced in the course of the preceding Analytical Operations.—From what has preceded it will be seen that the density of the current and the proportion of the free nitric acid necessary for the electrolytic separation of the lead in the state of binoxide, vary according to whether we have to deal with an alloy of copper or an alloy not containing this metal. We can easily see the reason for this difference by the following considerations:—In all the metals or alloys that we have experimented with, the lead has been brought to the state of nitrate, and we know that the normal electrolysis of this nitrate gives rise to the reaction—

$$(NO_3)_2Pb = \underbrace{N_2O_5 + O}_{\text{On the anode.}} + \underbrace{Pb}_{\text{On the cathode.}}$$

The deposit of lead in the state of binoxide (PbO_2) on the anode necessitates a supplementary supply of oxygen. In the case of an alloy not containing copper, this oxygen comes entirely from the electrolysis of the free nitric acid, $2NO_3H = N_2O_5 + O + H$. In the case of alloys of copper this oxygen comes on the one hand from the electrolysis of the nitrate of copper, $(NO_3)_2Cu = N_2O_5 + O + Cu$, and on the other hand from the electrolysis of the free nitric

* For 0·2 grm. of pure lead under the conditions described above the electromotive force should be from 2·6 to 2·7 volts.

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acid. We can easily see that in such a case the quantity of this acid present can be considerably diminished.

As to the difference of the density of the current, this is explained by the fact that the products separated at the cathode and the electrolytic reactions are very different in the presence and in the absence of copper.—*Bull. Soc. Chim.*, Series 3, vol. xiv. xv., No. 22.

PROCEEDINGS OF SOCIETIES.

CHEMICAL SOCIETY.

Ordinary Meeting, March 2nd, 1899.

Professor Dewar, F.R.S., President, in the Chair.

Mr. John S. MacArthur was formally admitted a Fellow of the Society.

Certificates were read for the first time in favour of Messrs. Clement Harrison Baker, Athelney, Featherstone Road, King's Heath, Birmingham; Frederick James Beale, Wilderspool Brewery, Warrington; Alfred Ernest Bond, Prince's Chambers, Corporation Street, Birmingham; Charles Robert Darling, 220, Eglinton Road, Plumstead; Percy Haigh, 312, Romford Road, Forest Gate, E.; Thomas Judge, 142, Waller Road, New Cross, S.E.; William McConnell, 178, Springfield Road, Glasgow; Wilfred Walter Morris, Newtown St. Boswells, Roxburghshire, N.B.; Maurice Emile Schweich, 85, Belgrave Road, S.W.; Edward Thomas Shelbourn, 1, Chalcot Crescent, Regent's Park Road, N.W.; Richard Threlfall, 45, Frederick Road, Edgbaston, Birmingham; Ernest Albert Tyler, Warsop, Mansfield, Notts.

Of the following papers those marked * were read:—

*35. "*Bromomethylfurfuraldehyde.*" By H. J. H. Fenton, M.A., and Mildred Gostling, B.Sc.

It has been shown by the authors in a previous communication (*Trans.*, 1898, lxxiii., 556) that certain carbohydrates, when acted on by hydrogen bromide in ethereal solution, give rise to a beautiful purple colouration. From observations made with a considerable number of typical carbohydrates, it would appear that the rapid production of this intense colour is characteristic of ketohexoses, or substances capable of yielding them by hydrolysis. The colour-producing substance has now been isolated in a pure state, and is obtained in the form of short, golden-yellow, prismatic crystals belonging to the oblique system. It melts at 60°, decomposes somewhat explosively at a higher temperature, and is practically insoluble in cold water, but dissolves easily in most organic solvents, giving solutions which powerfully stain the skin. Its solutions give a bright orange colour with aniline acetate after some time; they powerfully reduce silver and copper solutions, react with phenylhydrazine, and when treated with an ethereal solution of hydrogen bromide produce an intense purple colouration, which is exactly similar to, but appears even more quickly than, that obtained with ketohexoses. Analysis and molecular weight determinations show that it has the formula $C_6H_5BrO_2$, and its reactions and properties indicate that it is a bromomethylfurfuraldehyde,—

$$\begin{array}{l} H\cdot C{=}C-CHO \\ \quad\vert \quad\vert \quad\diagup O \\ H\cdot C{=}C-CH_2Br \end{array}.$$

On oxidation with silver oxide it yields ω-hydroxymethylpyromucic acid, identical with that obtained by Hill and Jennings from the corresponding bromo-acid (*Amer. Chem. Journ.*, 1893, xv., 162). The whole of the bromine is precipitated by an alcoholic solution of silver nitrate, and from the solution a substance is obtained which closely resembles, but seems to be isomeric with, the hydroxymethylfurfuraldehyde of Düll and Kiermayer (*Chem. Zeit.*, 1895, xix., 206, 1003); a similar result is obtained by heating the substance with water in presence of barium carbonate. If the substance be covered with water and saturated with sulphur dioxide, it slowly dissolves, and the solution, after remaining for some hours, gives, on extraction by ether, a product which crystallises from hot water in yellow needles; these melt at 117°, and in solution give a magnificent blue colour with caustic alkalis. Analysis and molecular weight determinations indicate that this is a condensation product, and is free from bromine; its constitution is now being investigated.

*36. "*The Reaction of Alkyl Iodides with Hydroxylamine. Formation of Alkylated Hydroxylamines and Oxamines.*" By Wyndham R. Dunstan, F.R.S., and Ernest Goulding, B.Sc.

As the authors have shown previously (*Proc.*, 1894, x., 138; *Trans.*, 1896, lxix., 839), methyl iodide readily reacts with hydroxylamine, forming hydriodides of hydroxylamine and the hydriodide of a trimethyl derivative. The hydrated base crystallises well, and melts sharply at 96°. It is not volatile. The anhydrous base has not yet been isolated. The aqueous solution is strongly alkaline, and does not reduce Fehling's solution. Solution of silver nitrate is only reduced on warming, or after prolonged standing. Dimethylamine and formaldehyde are produced by the action of hydriodic acid, but no methyl iodide. The same decomposition ensues when the base (or its salts) is heated either alone or with dilute sulphuric acid, $(CH_3)_3NO = CH_2O + NH(CH_3)_2$. When allowed to stand in aqueous solution in contact with zinc dust, it is reduced to trimethylamine, $(CH_3)_3NO + H_2 = (CH_3)_3N + H_2O$.

The principal salts of the base are described.

The authors conclude that this substance is not a true trimethylhydroxylamine, but a *trimethyloxyammonia* or *trimethyloxamine*, $(CH_3)_3N{:}O$.

By the reaction of methyl iodide with trimethyloxamine the iodide of a tetramethyl derivative is produced. The free base, which is strongly alkaline, has, so far, been obtained only in aqueous solution. The salts crystallise well.

When the solution of a salt is warmed with an alkali, methyl alcohol is split off and trimethyloxamine is formed, $N(CH_3)_3OCH_3OH = N(CH_3)_3O + CH_3OH$.

When the aqueous solution of a salt is heated at 150 in a closed tube, trimethylamine and formaldehyde are produced, $N(CH_3)_3OCH_3OH = N(CH_3)_3 + CH_2O + H_2O$.

When the iodide is heated with concentrated hydriodic acid, the products are methyl iodide, dimethylamine, and formaldehyde,—

$$N(CH_3)_3OCH_3OH + HI = NH(CH_3)_2 + CH_3I + CH_2O + H_2O.$$

When reduced in aqueous solution with zinc dust, trimethylamine and methyl alcohol are formed,—

$$N(CH_3)_3OCH_3OH + H_2 = N(CH_3)_3 + CH_3OH + H_2O.$$

The base is, therefore, *trimethylmethoxyammonium hydroxide*, $(CH_3)_3N\cdot OCH_3\cdot OH$.

When ethyl iodide reacts with hydroxylamine, hydriodides of hydrozylamine are formed, together with a *diethylhydroxylamine hydriodide*. The base is an oily liquid with a curious aromatic odour, boiling, with some decomposition, between 130—134°. Its aqueous solution is strongly alkaline, and acts as a powerful reducing agent. The salts are fully described; the oxalate, $[(C_2H_5)_2NOH]_2H_2C_2O_4$, crystallises very readily and melts at 136—137°. When heated it decomposes into ethylamine and acetaldehyde,—

$$(C_2H_5)_2NOH = C_2H_5NH_2 + C_2H_4O.$$

When heated with hydriodic acid, diethylamine is formed, but no ethyl iodide. It forms an acetyl derivative. The substance is, therefore, a true *β-diethylhydroxylamine*, $N(C_2H_5)_2OH$. It is isomeric with the two diethylhydroxylamines described by Lossen ($NHEtOEt$), but is probably identical with the substance obtained by Kissel

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by the action of zinc ethyl on nitroethane. The substance now described closely resembles in its decompositions the β-dibenzylhydroxylamine studied by Behrend and Leuchs.

By the reaction of diethylhydroxylamine with ethyl iodide, the hydriodide of a triethyl derivative is obtained. The base is crystalline and non-volatile. The aqueous solution is strongly alkaline. It does not reduce Fehling's solution, but reduces silver nitrate on warming. The principal salts are fully described. In all its reactions this base closely corresponds with trimethyloxamine. When heated it breaks up into diethylamine and acetaldehyde; when reduced with zinc dust in aqueous solution it furnishes triethylamine, whilst by the action of hydriodic acid it is converted into triethylamine without the formation of ethyl iodide. This substance is, therefore, *triethyloxyammonia* or *triethyloxamine*, $(C_2H_5)_3N{:}O$. It is not identical with the isomeride of triethylhydroxylamine which Bewad describes as resulting from the action of zinc ethyl on nitroethane.

Similarly, normal propyl iodide and secondary propyl iodide react with hydroxylamine, forming *dipropyl-* and *di-isopropylhydroxylamines*, $(C_3H_7)_2NOH$.

Hantzsch and Hilland (*Ber.*, 1898, xxxi., 2058) have recently described their work on this subject. They generally confirm the account given by the authors five years ago of the reaction of methyl iodide with hydroxylamine. They assert that the hydrated base (see above) is really a carbonate. The authors have repeated their experiments, and find that there is no foundation for this statement. It is evident, from the different account given by Hantzsch and Hilland of the properties of trimethyloxamine, that the material they examined contained impurity, probably hydroxylamine.

By the reaction of ethyl iodide with hydroxylamine, Hantzsch and Hilland obtained only monethylhydroxylamine hydriodide. The authors have repeated their experiments, and have been unable to isolate any such substance. They find, as stated above, that diethylhydroxylamine is the chief product of the reaction.

Discussion.

Dr. Hewitt drew attention to Bamberger's recent discovery of the analogous dimethylaniline oxide by the direct oxidation of dimethylaniline by hydrogen peroxide (*Ber.*, 1899, xxxii., 342). The substance is destitute of reducing properties, and exhibits a peculiar transformation into a mixture of ortho- and para-nitrodimethylanilines by the action of nitrous acid. This transference of an oxygen atom from the dimethylamino- to the nitroso-group, thereby converting it into a nitro-group, may possibly be the analogue of the conversion of trimethyl oxamine into a mixture of dimethylamine and formaldehyde.

Dr. Forster remarked that distillation under atmospheric pressure resolves the benzyl ether of camphoroxime into benzaldehyde and camphorimine, a change suggesting analogy with the conversion of trimethyloxamine into formaldehyde and dimethylamine.

37. "*Derivatives of αα'-Dibromocamphorsulphonic Acid.*" By Arthur Lapworth.

When ammonium α-bromocamphorsulphonate is heated with bromine and water at 110—120°, a dibromocamphorsulphonic acid is produced, identical with that obtained in small quantities by heating the salt with dilute nitric acid (*Trans.*, 1897, lxxi., 19; compare *Proc.*, 1898, xiv., 159), and its investigation has been continued with the following results:—

The *ammoninm*, *potassium*, *sodium*, *calcium*, *barium*, *zinc*, *cadmium*, and *lead* salts are readily soluble in water and crystallise well; the *basic lead* salt is amorphous, and is practically insoluble in water. *αα'-Dibromocamphorsulphonic chloride*, $C_{10}H_{12}Br_2O{\cdot}SO_2Cl$, is very sparingly soluble in the usual media; it crystallises in beautiful hemihedral forms belonging to the orthorhombic system, is isomorphous with the sulphonic bromide already described (*loc. cit.*), and melts at 203—204° with decomposition. The *amide*, $C_{10}H_{12}Br_2O{\cdot}SO_2NH_2$, forms hemihedral crystals, is very sparingly soluble in the ordinary media, and melts at about 238° with decomposition.

When *αα'*-dibromocamphorsulphonic chloride is treated with piperidine in ethereal solution, a mixture of *dibromocamphorsulphopiperidide*, $C_{10}H_{12}Br_2O{\cdot}SO_2NC_5H_{10}$, and *monobromocamphorsulphopiperidide*,—

$$C_{10}H_{14}BrO{\cdot}SO_2NC_5H_{10}$$

is obtained. The former crystallises in orthorhombic plates or prisms melting at 157—158°; the latter, which may also be obtained by the action of piperidine on *α*-monobromocamphorsulphonic chloride, crystallises in plates melting at 152°.

When dibromocamphorsulphonic acid is heated with strong alkalis, bromine is eliminated, and the product, on treatment with phosphorus pentachloride, yields α-monobromocamphorsulphonic chloride melting at 135°, the action being exactly analogous to that of alcoholic potash or soda on *αα'*-dibromocamphor.

When heated at its melting-point, *αα'*-dibromocamphorsulphonic bromide loses sulphur dioxide, yielding *αα'π-tribromocamphor*, $C_{10}H_{13}Br_3O$. This crystallises from dilute alcohol in fine needles and melts at 69—70°; it is rapidly decomposed when warmed with solutions of silver salts or with alkalis, the product with the latter being *απ*-dibromocamphor melting at 152°. The new tribromocamphor is also obtained by heating *απ*-dibromocamphor with bromine at 120° in sealed tubes; this fact and others which have been mentioned indicate that the dibromocamphorsulphonic acid has the constitution assigned to it by the author.

38. "*Ethylic ββ Dimethylpropanetetracarboxylate.*" By W. Trevor Lawrence.

Meyenburg (private communication, compare *Ber.* 1895, xxviii., 785) attempted to prepare ethylic ββ-dimethyl propanetetracarboxylate by the condensation of ethylic isopropylenemalonate with ethylic sodiomalonate, but was unsuccessful, and, with his permission, the author has continued the work.

Ethylic ββ Dimethylpropanetetracarboxylate,—

$$CMe_2[CH(CO_2Et)_2]_2,$$

is formed in small amount in preparing ethylic isopropylenemalonate from acetone and ethylic malonate in the presence of acetic anhydride and zinc chloride. It is obtained readily by the interaction of molecular quantities of ethylic isopropylenemalonate with ethylic sodiomalonate in dry ethereal or benzene solution. The mixture is allowed to boil during twenty-four hours, a half molecular proportion of ethylic sodio malonate added, and the boiling continued during a further twenty-four hours. On fractional distillation in a vacuum, the compound is obtained as a thick oil boiling at 218° under 14 m.m. pressure. On hydrolysis with alcoholic potash it is converted into ββ-dimethylpropanetricarboxylic acid, $CO_2H{\cdot}CH_2{\cdot}CMe_2{\cdot}CH(CO_2H)_2$, melting at 172°, and with sulphuric acid into ββ-dimethylglutaric acid,—

$$CO_2H{\cdot}CH_2{\cdot}CMe_2{\cdot}CH_2{\cdot}CO_2H,$$

melting at 101°, from which the anhydride melting at 123° was obtained.

The author is engaged with Dr. Herz in the further investigation of the properties of the substance.

(To be continued).

PHYSICAL SOCIETY.

Ordinary Meeting, March 10th, 1899.

Prof. Oliver Lodge, F.R.S., President, in the Chair.

Mr. A. A. Campbell Swinton described and exhibited the Wehnelt Current-interrupter.

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A glass cell contains a large cylindrical negative electrode of lead and a small positive electrode consisting of a platinum wire about $\frac{1}{16}$ inch or $\frac{1}{8}$ inch in length in a solution of 1 part sulphuric acid to about 5 parts water. The platinum wire may project from the top of the shorter arm of a J-shaped ebonite tube, so that it can point upwards immersed in the solution. Or it may be fused into a similar glass tube; but glass is apt to crack in the subsequent heating. Wehnelt's interrupter replaces the make-and-break apparatus of an induction coil; it also replaces the ordinary condenser of that apparatus. In its present form it requires rather a strong current. The resulting spark at the secondary terminals differs in character from the ordinary spark of an induction coil; it is almost unidirectional, and in air takes a Λ form—bright, continuous, and inverted—somewhat like a pair of flaming swords rapidly crossing and re-crossing one another at their points. By blowing upon the Λ it breaks up, and then more nearly resembles the customary discharge of a coil. The sound emitted by the spark has a pitch that varies with the conditions of the circuit. As the self-induction of the circuit is diminished, the spark-pitch rises; it becomes infinite when the self-induction vanishes, *i.e.*, the Wehnelt interrupter will not work in a circuit devoid of self-induction. As the applied potential-difference diminishes, the spark-pitch diminishes. In Mr. Campbell Swinton's experiments, 25 volts was the minimum primary voltage at which his apparatus would work. The spark-pitch also varies with the length of the platinum wire electrode in the solution. If the circuit is closed by dipping this electrode into the solution, the apparatus will not work; the wire must be dipped in before closing the circuit. After working for about a quarter of an hour, the action often ceases; this fatigue-effect is not due to heating of the solution, for it is not obviated by keeping the temperature constant by a water-bath. It is supposed that the oxygen generated at the platinum electrode forms a more or less insulating film which interrupts the current until absorbed by the surrounding water. The fact that oxygen is more easily absorbed than hydrogen may explain why it is necessary to connect the platinum electrode to the positive pole of the battery or dynamo. When the platinum electrode is dipped gradually into the solution, the wire gets red-hot, and the interruptions do not take place. Again, when the apparatus stops from fatigue the platinum gets red-hot. The action is further complicated by a series of small explosions, and by the formation of a kind of electric arc at the platinum electrode. The coil exhibited was connected to the 100-volt electric light mains at Burlington House; in this case the potential difference at the terminals of the primary was 30 volts, and that across the interrupter 150 volts—a total of 180 volts, showing the effect of impedance. For Röntgen ray work the apparatus would be very effective, but unfortunately the sparks produce great heating, so that the cathodes of tubes are melted. Mr. Campbell Swinton suggested that, as the sparks were more nearly continuous than ordinary discharges, they might produce Hertz waves less rapidly attenuated than those now applied to wireless telegraphy; the trains of waves would also follow one another at shorter intervals than those from the sparks at present employed.

The PRESIDENT said he was rather surprised that the self-induction of the primary coil was not sufficient of itself to form the induction factor in the impedance necessary for perfect working. He would like to know how the apparatus behaved when an alternating current was used. Did the secondary coil become damaged by overheating? Did reversal of the current assist the recovery from the fatigued condition of the apparatus? The natural period of the circuit depended upon its capacity and its self-induction. There was undoubtedly capacity at the surface of the platinum electrode in the liquid; this capacity acted together with the auxiliary self-induction and the self-induction of the rest of the circuit in the orthodox way, and there was automatic adjustment of resonance to the frequency of the interruptions, probably by variations of the capacity at the electrode. The heating effect when a wire was made to close a circuit with a liquid was discovered many years ago.

Prof. G. M. MINCHIN thought that the usefulness of the apparatus would be greatly increased if it could be made to work with less current. He had himself succeeded with 12 applied volts, but not with 10 volts. As a tentative experiment he had used a horizontal lead plate—with disastrous effect, for the apparatus went suddenly to pieces. Explosions were frequently obtained, but they were not attended with much real danger. In a later and safer apparatus he used a platinum wire about $\frac{1}{2}$ inch long, projecting from a glass tube, around which the lead plate was bent. There appeared to be a definite depth of immersion of this wire, at which the apparatus worked with minimum current. In his apparatus, this critical position was when half the wire was below the surface of the liquid, the other half projecting into the air. He attributed the fatigue to the presence of gas about the electrodes, for he observed that a mechanical tap to the base of the apparatus restored the working condition.

Mr. ROLLO APPLEYARD pointed out that the improved result at half immersion observed by Prof. Minchin, taken together with the phenomena described by Mr. Campbell Swinton as to the effect of dipping the electrodes into the solution, suggested that the liquid immediately around the submerged part of the wire was at some instants in the spheroidal state. The breaking-down of the spheroidal state would be facilitated by heat lost by the immersed part to the non-immersed part of the wire. The capacity for heat of the non-immersed part, and the degree of roughness or smoothness of the immersed part, would thus appear as factors in the explanation. No doubt the evolved gases were the primary cause of the interruption of current, but the wire having once become red-hot the spheroidal condition would introduce a further cause of electrical separation between the wire and the liquid.

Prof. V. BOYS asked whether it was the liquid or the electrodes that became fatigued. Experiments should be made to determine the effect of variations in the hydrostatic pressure around the platinum electrode.

Mr. T. H. BLAKESLEY said that the rise of potential at the terminals of the interrupter proved that the arrangement possessed capacity. Such a rise of potential could not occur without there being capacity any more than it could without self-induction.

Mr. D. K. MORRIS described experiments he had made with a Wehnelt interrupter, using a 1 kilowatt transformer with a transformation of 4 to 5, intended for 10 ampères at 100 volts. The anode of the interrupter was designed to have an adjustable surface to correspond with the load on the secondary—a platinum wire at the end of a copper wire could be projected more or less through the drawn-out lower end of a glass tube containing oil. The best results with the interrupter were obtained with about 45 volts on the primary circuit. At this pressure, an average current of 1 ampère sufficed to give 125 (alternating) volts very steadily on the secondary. As measured by an electrostatic instrument, the "no-load" loss was only 45 watts. The secondary could then be loaded up with lamps, provided that the exposed surface of platinum wire was proportionately increased. The energy delivered to the lamps, however, was not at any load much greater thon 45 per cent of that taken from the mains. By connecting the interrupter with a condenser of $\frac{1}{4}$ microfarad, the efficiency at small loads was increased to nearly 60 per cent. He had observed that the fatigue of the interrupter could be temporarily remedied by reversing the current.

Mr. C. E. S. PHILLIPS asked whether Mr. Campbell Swinton had tried other liquids than dilute sulphuric acid. So far as his own experiments went, he had only obtained good results with that electrolyte.

Mr. CAMPBELL SWINTON, in reply, said that with the apparatus arranged in a simple circuit an alternating

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current applied to the primary of an induction coil through a Wehnelt interrupter produced only about half the effect of the corresponding direct current—apparently only half the alternations got through. But if two interrupters were connected in parallel circuits, it was possible so to arrange them that one took one half and the other the second half of the alternations. It might therefore be possible to design an induction coil with two primary windings to correspond to the two interrupters, so as to give an additive effect. The induction coil he had used had suffered no damage from the currents employed in the experiments exhibited; there was extremely little heating of the secondary. He could not with his apparatus restore the working condition by any mechanical disturbance of the interrupter. Hydrochloric acid failed, but a saturated solution of potassic bichromate gave fair results.

The PRESIDENT, in proposing thanks, said he did not agree with Mr. Campbell Swinton's remarks as to the chances of improving Hertzian telegraphy by the use of these interrupters. The rate of interruption with this apparatus was something like 1000 per second, but the vibrations corresponding to Hertz waves were of the order 100,000 per second. The wave-trains from oscillations excited by the new interrupter would still be series of damped vibrations; the amplitudes would not be maintained. It might be advantageous to have sparks following one another so rapidly, but he doubted it. For Hertzian telegraphy, the spark at the oscillator should "crackle"; to produce the best effect, the air about the oscillator should be in a non electric condition.

A paper by Mr. A. GRIFFITHS on "*An Apparatus for the Determination of the Rate of Diffusion of Solids dissolved in Liquids*" was then read.

The apparatus consists of a cylindrical glass vessel subdivided about midway by a horizontal non-porous partition into which are fitted a number of vertical tubes. The lower section of the vessel is filled with a liquid, such as an aqueous solution of cupric sulphate, and the upper one contains pure water. The method consists in determining by chemical analysis the quantity of cupric sulphate transmitted up the tubes. The paper gives the theory of the method, with very few experimental results. Ordinary diffusion observations are affected by the flow of liquid in the tubes due (1) to changes of temperature of the apparatus as a whole, (2) to differences of temperature throughout the liquid, (3) to local variations in volume produced by the process of diffusion, (4) to inequalities in the lengths of the tubes. Equations are given for determining the magnitudes of the sources of error, and certain numerical cases are worked out.

The same author also contributed a note on "*The Source of Energy in Diffusive Convection.*"

Diffusion tends to produce local changes of density, causing gravitational currents, which currents can be made to do work. By "diffusive convection" the author means these gravitational currents. The heat equivalent of the work done is determined in a particular case, *i.e.*, for a sub-divided vessel, as in the above paper, having two tubes of unequal length. He points out that the heat absorbed, owing to diffusion through one of the tubes, is independent of the mechanical motion of the liquid in that tube, and it is also independent of the length of the tube.

The PRESIDENT proposed a vote of thanks, and in doing so described an apparatus he had used for a thermostat. A double-walled cylinder of copper sheet, with a little water in the inter-space, is exhausted at atmospheric temperature until the water boils; it is then sealed up. Water-vapour is a powerful equaliser of temperature, and a vapour jacket of this kind is very efficient when it is required to maintain uniform temperature—not constant temperature.

Mr. WATSON described the method of Mr. E. H. Griffiths, who used tap-water as a negative source and a gas flame as positive source—with extremely good results—as a thermostat for constant and for uniform temperature.

The meeting then adjourned until March 24th.

ADDRESS OF THE PRESIDENT,
Prof. OLIVER LODGE, D.Sc., F.R.S.
February 10th, 1899.

IN taking the Chair of this Society for one year, notwithstanding that I am a country member and therefore shall not be able always to be present, I am I daresay traversing the views of what is considered best for the Society by a minority of members. I have no knowledge that it is so, but it can hardly be otherwise. I hesitated myself for some time, but ultimately consented to be put in nomination by the Council; and I can promise that I shall try to be present as often as my duties permit.

I have been a member of the Society from its earliest infancy, for though not technically an "original member," nor one admitted in the first year, that is a mere accident of not having presented myself for admittance by the Chair; perhaps I had not paid my subscription, but I used to attend all the meetings, and my memory goes back to the preliminary discussions that preceded the birth of the Society, between Prof. Foster, Prof. Adams, Dr. Gladstone, Dr. Atkinson, and Dr. Guthrie, especially Dr. Guthrie, and to whom the idea of the Society was, I believe, largely due.

In those days we used to meet at South Kensington on Saturday afternoons; and my experience of recent years is altogether too remote and detached to make me aware whether the change, from the hospitable laboratory at South Kensington to the no doubt equally hospitable but less *physically* inspiring quarters of Burlington House, has been an unmixed advantage. If it is an unmixed advantage, the Society has been fortunate.

Our death-roll for the past year contains the names of two original members whose figures were familiar at the meetings in those early days: Henry Perigal and Latimer Clark. It also contains the names of Sir J. N. Douglass, so well-known in connection with lighthouse work; of Dr. Obach, the skilled electrician and designer of Messrs. Siemens Bros.; of the Rev. Bartholomew Price, known not only as a mathematician but also as a man of public spirit and enterprise in the University of Oxford, who had I believe more to do with the early financial success of the Clarendon Press than is generally known; of Dr. J. E. Myers, and alas! of Dr. John Hopkinson.

It is unfitting that this year's deliverance from the Chair of any Society of which John Hopkinson was a member should fail to contain some reference to his untimely loss; yet there is nothing for me to say but what you already feel, and no words of mine are needed. I cannot say that I knew him in his youth, but I heard of him. He and I as self-taught students—at least, I was at that time self-taught, and he could hardly have found a better teacher than himself—once figured together in the so-called honours list of the South Kensington May examinations in Electricity and Magnetism, or else in Sound, Light and Heat, or in both. Needless, to say, his name stood above mine. He passed, for fun, in nearly the whole range of South Kensington subjects; I took a good many of them, but had nothing like either his comprehensive range or his educational advantages. And then he went and wrested the Senior Wranglership from that exceptionally brilliant mathematical genius, J. W. L. Glaisher. That was a surprising achievement for a Whitworth Scholar and practical Engineer. May I be allowed to congratulate Mrs. Hopkinson and her family not only on a peculiarly noble donation, but also on its special application to the welding together the names of Cambridge, of Engineering, and of Hopkinson.

It is remarkable, as Mr. Arthur Balfour said in a speech the other day (at the opening of the Battersea Institute, I

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think), it is remarkable how in modern times the pursuit of science tends in the direction of rapid and immediate application.

In Newton's time pure science was altogether aloof from practice: I do not suppose that the gravitational theory of astronomy had any effect on His Majesty's coins at the Mint, nor did the prismatic sifting of white-light lead at that time to any chemical applications of spectrum analysis. Even as late as Faraday's day the induction of currents by motion and magnetism exercised no appreciable effect on commerce and industry.

Nowadays, Fourier's theorem is applied by Lord Kelvin to work on Atlantic cable; Hopkinson's researches on the magnetic circuit (an idea that has revolutionised the practical treatment of magnetism) result at once in improvements in the dynamo; and Hertz's experimental detection of Maxwell's waves seems likely to result before long in a new system of wireless telegraphy.

What is the cause of this keen interest in practical applications felt in varying degrees by nearly all modern physicists, felt most keenly and consistently I think, of those I know, by your past-President Prof. Ayrton? Is it the example and inspiration of Lord Kelvin, or is it that the human race generally is beginning to be better educated than it used to be, to take more kindly to the result of scientific researches, to be more eager to learn about them, and, if possible, to apply them; partly, no doubt, because it has gradually discovered that by judicious treatment it can convert them into substantial commodity?

Surely, on the whole, with some drawbacks, the result from the point of view of science is good. If science were really remote from all human use or interest, as some scoffers still endeavour to maintain it to be, would there not be a fear lest gradually the human race should get tired of it, should cease to encourage even by approval or applause those whose instinct or mission it might be to develope it? So that gradually a blight might settle down, and advanced scientific knowledge become as extinct as a dead language or a fossil genus. A few scholars here and there would take an interest in it, as they did in the Middle Ages, and it might perhaps for a time be instilled into youth at the point of a cane, as the dead languages not so long ago used to be; but unless a branch of learning enters in some way into the life and well-being of a community, unless it has some real interest—a literary interest it may be, a commercial interest perhaps, a living human interest of some kind—there is fear that, however artificially bolstered up it may be for a time, by those whose stock in trade it is and who know little else, it will ultimately be suffered to go by the board and become to all practical intents and purposes dead, buried, and extinct.

I said just now that I supposed the public as a whole were gradually getting better educated, but how miserably slow is the process and how lamentable the present result. I have no feud with orthodox secondary schoolmasters, indeed some of them are my very good friends, but is it not painful to be unable to speak to the average so-called educated Englishman (except a few here and there of course) on any scientific discovery without at once being met by a hopeless wall of ignorance?

Is it so in other countries? I hardly think so; I do not think it is so marked even among Scotchmen, at any rate not among Scotchmen who have had their Natural Philosophy year at the University. A year for training in the whole of science—it is not much. If scientific men were ignorant of letters in the same proportion they would hardly be able to read, except in words of one syllable, nor write, except with the laborious contortions of the village urchin; a year extended on the subjects of all the Arts would not carry one very far. And as to sums, how many men there are whose mathematical equipment is limited to the practice of compound addition and subtraction, and who shy if they see an algebraic symbol, even in a newspaper—indeed, when they occur in newspapers they are often of a kind that deserve to be shyed at.

They learn languages, some people seem to enjoy learning foreign languages—though the multiplicity of them is an artifical arrangement which an international convention might alter if it choose—but the exact and beautiful language in which a great part of science is and must be written is to the majority of men unknown. Are teachers wholly free from blame in respect of the dislike which many boys feel for the most elementary mathematics, for problems which may be made exhilarating when properly presented? I believe they are not. If the teacher dislikes mathematics, the boys will hate it, and if they hate it when young they will love it but little better when they grow up and proceed to be teachers themselves. There is a law of geometrical progression or compound interest here, and it seems to have been at work for some time. I must not, however, be understood here to be speaking of really cultivated intelligences or authorities in any subject. A thorough training in any branch of knowledge may so stimulate and enlarge the faculties as to fit them for intelligent appreciation and criticism of many other branches. Some men of letters I know whose minds are copiously and essentially scientific, they have not the detailed knowledge of the professed worker in science—that would be impossible and unnecessary—but they appreciate and assimilate all the main doctrines of science, and their broad criticisms and suggestions are often of value to the special worker. Any educational strictures on which I have ventured have reference not to scholars but to average people; at the same time I believe many scholars feel their deficiency in mathematics, and I believe it to be the result of bad teaching.

This is not my Address, it is a preliminary excursus, my Address has reference to a physical problem which has interested me, and about which I thought it might be interesting if I said something. It is customary to review some topic in an Address, not to adduce anything specially new, but to treat of or attempt to clarify something already known. Usually it is some experimental fact which is thus treated, sometimes it is a point of theory; it is the latter to which I wish to ask your attention.

As to experiments, if I quickly review some of those that strike me in the past year—there is further progress to be reported concerning the developments of Prof. Zeeman's great discovery, the most important being (1) the new manifestations of it, or of a closely allied phenomenon, discovered by Professor Righi, to which Prof. S. P. Thompson called the attention of Section A at Bristol last September; and (2) some extension of the resolution of complex lines, discriminating between the effect as exhibited by different lines, a discrimination which seems likely to lead to an extension of the powers of spectrum analysis by the application of a magnetic field to the source of light, as studied with apparatus of splendid dispersive power by Prof. Preston, and with his own ingenious method by Prof. Michelson. There is a notable continuation of the remarkably powerful and beautiful researches into atomic properties carried on at Cambridge by Prof. J. J. Thomson; about which a great deal more might be said. And then there is the prediction made in the columns of *Nature* by Prof. G. F. FitzGerald, but not yet verified, that circularly polarised light sent through an absorbing medium would constitute a magnet.

Many have been the attempts, from Faraday downwards, to excite magnetisation by means of light, to detect a real and not an imaginary "magnetisation of a ray of light," but all the experimenters hitherto have failed to realise the necessity of an absorbent medium. The effect is bound to be small, and of course it may not be there after all, but I understand it is being looked for, and it has at any rate been on rational grounds predicted.

Dr. Barton has continued experiments on the damping of waves on wires, and has not yet reconciled a discrepancy between theory and experiment; being able, as I understand him, to account for only 5½ per cent of the out-

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standing discrepancy. I have not myself looked into the matter, but I understand that a note has been communicated by Mr. Heaviside. I hope it will be published in full.

The subject of Terrestrial Magnetism, in the hands of Prof. Schuster on the theoretical side and of Prof. Rücker on the practical side, has recently entered on an enlarged existence, and seems to be taking up a position almost of an independent science, so that when the multifurcation or explosion of Section A occurs, as sooner or later I fear it must, the fragment entitled Meteorology and Terrestrial Magnetism will perhaps not be one of the smallest.

The publication called *Science Abstracts* has continued to be welcomed by workers all over the country, and the abstracts sent by Mr. Fournier d'Albe to the *Electrician* are also useful and admirably done. I have no knowledge myself of the mode of control of the publication of our *Science Abstracts*, but I confess to a personal preference for the older form, the one with a less startling cover, and with a list of authors' names, instead of unnecessary advertisements of well-known firms, on its back page. Undoubtedly the inauguration of these *Abstracts* supplies a long-felt want, and even if one does not always find time to read them it is a comfort to feel that there they are, to be read in some less pressing season; and one need not envy the German worker his *Beiblätter* as one used to.

But there is one most important event that has occurred during the year, perhaps to us conjointly as physicists the most important of all, an event of which the science of Physics will feel the effects—I trust the wholly favourable effects—for centuries to come: I mean the decision of the Government to begin on a small scale the inauguration of a National Physical Laboratory. If its effects are ever in any respects unfavourable to true science, a heavy indictment will lie against its future governing body, and against its Superintendtent or Physicist Royal.

I wish to congratulate Sir Douglas Galton, as well as to some extent myself, on the result, the speedy result, of our urging of the subject, within the present decade, on the British Association; and as a Physical Society I think we owe a debt of gratitude to the Committee appointed by the Treasury to examine into the question, whose members gave themselves an immense amount of trouble, travelling to Berlin and elsewhere to make themselves acquainted with foreign ideals, and altogether going into the subject with extreme thoroughness, scientific judgment, and public spirit. The chairman of the Committee was Lord Rayleigh, but during his absence in India the acting Chairman was constantly Professor Rücker, Mr. Chalmers represented the Treasury with urbane frugality, and to Prof. Rücker and Mr. Chalmers, as well as to the other members of the committee, I am sure you will agree with me our thanks are justly due.

The record of their labours and of the voluminous evidence which they obtained, to which evidence indeed several of us here contributed, is embodied in a Blue Book of more than usual interest and instruction. I commend the perusal of it not only to professed physicists, but to all scientific teachers and their advanced students, that they may learn what accuracy is, and what it is practically wanted for.

It is not for me as your President to touch at any length upon outside or political topics, but briefly I venture to think that the year 1898 has been a year of no ordinary good fortune, at least to the Anglo-Saxon race. A year, and a Government, which has witnessed and assisted not only the beginning of a National Physical Laboratory, but such great outside events as the Imperial expansion and co-operation of America (for America, and not the United States, it will now have to be called), the liberation of Crete, and the restoration of the civilisation of Upper Egypt, is a year upon which we can look back with satisfaction, and is a Government which, irrespective of party, we may legitimately congratulate, and even—though that I admit is unusual—thank.

Would that we could add to its laurels the commencement on wise lines of a real and comprehensive, dignified and progressive, genuine University of London.

NOTICES OF BOOKS.

The Elements of Physical Chemistry. By J. Livingston R. Morgan. New York: John Wiley and Sons. London; Chapman and Hall, Ltd. 1899. Pp. viii.—292. 12mo., cloth.

In this volume the author has undertaken to present the elements of the entire subject of Physical Chemistry in a compact treatise, together with the important and but little known applications of it to the other branches of chemistry. The treatment is of course mathematical, yet the calculus is only used in the derivation of some of the laws, and the book can be used by students not proficient in higher mathematics. The author acknowledges indebtedness to the works of Ostwald, Le Blanc, and Nernst, and makes no claim to originality, but he has succeeded in making some of the topics simpler and clearer than usual.

Chapters are devoted to the three states of matter, solution, the *rôle* of ions, thermochemistry, chemical kinetics, phases, and electrochemistry; the last-named being discussed in four sections—migration of ions, conductivity of electrolytes, electromotive force, and electrolysis and polarisation.

Dr. Morgan defines Physical Chemistry as "that branch of the science of chemistry which has for its object the study of the laws and theories governing chemical phenomena"; he prefers the term "Physical" to "Theoretical" chemistry, because the subjects treated lie in the border land between physics and chemistry, and because purely physical methods are used.

The volume is especially adapted to the use of undergraduates in Columbia University, New York City, but it also appeals to a much larger audience; it contains no descriptive chemistry, which is assumed to be known to those undertaking the study of this work. Students who master its contents will find the study excellent mental discipline, and will gain a higher idea of modern chemical philosophy than can be acquired from any one text-book bearing on the subject known to the writer. The book seems well adapted to the needs of electricians who would learn the modern aspects of chemistry in its relations to electricity.

A perusal of the chapter on Solutions shows strikingly the greatness of the mind of Faraday; although his conception of ions has been modified by Grotthus and by Arrhenius, the English philosopher has the honour of taking the first step in the right path.

Dr. Morgan's book is well printed, and is furnished with an Index. H. C. B.

Chemistry in Daily Life. Popular Lectures, by Dr. Lassar Cohn, Professor in the University of Königsberg. Translated by M. M. Pattison Muir, M.A., Fellow of Gonville and Caius College, Cambridge. Second Edition, Revised and Augmented. London: H. Grevel and Co., 33, King Street, Covent Garden, W.C.

This book is said to embody the *substance* of a course of lectures delivered by the author to a Society in Königsberg. On looking through the Table of Contents one cannot but be struck with the immensity of the knowledge embraced; in fact, the book seems to be a kind of encyclopædia of physical and chemical technology. Considering its moderate size, the natural result is a collection of very condensed scraps of information upon many subjects, in our opinion too far advanced to be of much interest to the general reader, and too meagre to be of value to the student. As an instance of the condensation

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of the matter, on page 23, following a description of candles, the reader is introduced to the chemical elements, and within three short pages is involved in the composition and formula for methane, ethane, and propane! After a flying glance at photography there follows a description of Röntgen rays, which is singularly incomplete and not at all accurate; the author seems to have got into a tangle of Geissler tubes, millionths of an atmosphere, and cathode rays; an incorrect drawing is given to show the paths of the cathode and Röntgen rays from a tube that is now obsolete, and "the celebrated glass-blower Geissler" and "Röntgen" are the only names mentioned in the matter. Within three pages of this we find ourselves in the depths of bimetalism! One cannot help thinking that such hasty scraps of information, although perhaps in keeping with the spirit of the age, are of but little lasting value, either to the student or to the general reader.

Report of the Principal Chemist upon the Work of the Inland Revenue Branch of the Government Laboratory. For the Year ending 31st March, 1898. London: Darling and Sons. 1898.

The number of analyses and examinations made during the year amount to 65,313; this is a slight increase over the previous year. The business of the Laboratory is divided into two parts, viz., work in connection with the Revenue Department, and work in connection with other Departments.

The work connected with the Revenue Department has largely to do with beer, spirits, and tobacco; 11,018 samples of wort in various stages of fermentation were examined, besides 4436 samples of finished beer. Of the 60 samples of tobacco examined for adulteration, 35 were found to be genuine and 25 adulterated. The adulterated samples were of foreign manufacture, being either smuggled cake Cavendish or cut tobacco, bearing no label; 11,817 samples were examined for moisture.

The consumption of tobacco per head of the population appears to be steadily though slowly increasing, it being for the year dealt with in this report at the rate of 1 lb. 12½ ozs.

Legal proceedings have been taken 414 times in respect to samples analysed in this Department, and the total penalties inflicted have amounted to £6517; 119 cases were for selling so called "Temperance" drinks containing an excess of proof-spirit.

In other Departments the number of samples examined was 3480; these include a very miscellaneous lot of articles, such as butters, paints, cements, paper, water, &c.

CORRESPONDENCE.

ABSTRACTS OF CHEMICAL PAPERS.

To the Editor of the Chemical News.

Sir,—The German Chemical Society having recently done away with the abstracts formerly published in the *Berichte*, and having acquired control of the *Chemisches Centralblatt*, the result has been a decided cheapening of both journals, to the advantage of everyone concerned.

In my opinion, and in that of many of my American colleagues, there is need for a first-class publication which will be for all English reading chemists, irrespective of nationality, what the *Centralblatt* is for Germans. The Chemical Society of London, in its Abstracts, issues a good synopsis of current literature; but this is practically inaccessible to most American chemists, who cannot afford to pay the rather high subscription price of 30s., which includes the *Transactions*. For us to duplicate the work would be sheer waste of energy; the London Society might consent to issue its Abstracts under separate cover, and at a separate and reasonable subscription price for non-members. Still better, the work might be undertaken conjointly by the London Society and the American Chemical Society. The American Society might, for example, supply the abstracts of American literature, which is already quite extensive, as may be seen by referring to the monthly review of American research published in our *Journal*. Joint publication would enable the American Society to urge upon its fourteen hundred members the advantages of subscribing for the "English Centralblatt," and thus considerably increase the circulation and diminish the cost. About one-half the members of the German Society take the *Centralblatt*, and it is to be expected that several hundred subscribers for a similar English publication might be obtained outside of Great Britain, if the matter were properly pushed.

I am prompted to make these suggestions by the fact that this subject is being agitated in this country, several local sections of the American Chemical Society having already expressed a desire for co-operation with the London Society.—I am, &c.,

H. N. Stokes,
President of the Washington Section,
American Chemical Society.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

Note.—All degrees of temperature are Centigrade unless otherwise expressed.

Comptes Rendus Hebdomadaires des Séances, de l'Académie des Sciences. Vol. cxxviii., No. 7, February 13, 1899.

Heat of Formation of Anhydrous Lime.—Henri Moissan.—This constant has already been determined by Thomsen, who states the value to be +131·5 cal. This is, however, probably inaccurate, owing to the impurity of the calcium used. The author re-determined this constant by using pure calcium, which he prepared. The small crystals were placed in a cylindrical tube of platinum covered with a number of small openings a quarter of a millimetre in diameter. When the cylinder is placed in the calorimeter, a very little water enters, and the liberated water prevents the too rapid ingress of the water. It was found that 1 grm. of calcium was completely attacked in three or four minutes. The calcium was weighed previously, and also estimated as lime in the water of the calorimeter: $Ca+2H_2O=H_2+CaO_2H_2$ (sat. sol.). The heat of formation being 94·10 (mean of two determinations). From this can be deduced the heat of formation of anhydrous lime directly from its elements.

$Ca+O=CaO$ anhydrous	x cal.
$CaO+Aq=CaO_2H_2$ sat. sol.	+18·1 ,,
$H_2O=H_2+O$	−69 0 ,,
$Ca+2H_2O=CaO_2H_2$ sat. sol. . ..	+94·1 ,,

$$\therefore x + 18{\cdot}1 - 69 = 94{\cdot}1.$$

$$x = 145 \text{ cal.}$$

This number is considerably greater than that found by Thomsen.

Phosphorescent Strontium Sulphide prepared from Carbonate of Strontium and Sulphur Vapour.—J. R. Mourelo.—The apparatus used for the preparation of this substance consists of a long porcelain tube placed in a combustion furnace. Inside are two porcelain boats some distance apart. In one of these is sulphur in little pieces, and in the other natural strontium carbonate (strontianite) coarsely powdered. One end of the tube communicates with a nitrogen apparatus. The whole apparatus must be filled with dry nitrogen before the heating begins. The tube is then gradually heated, be-

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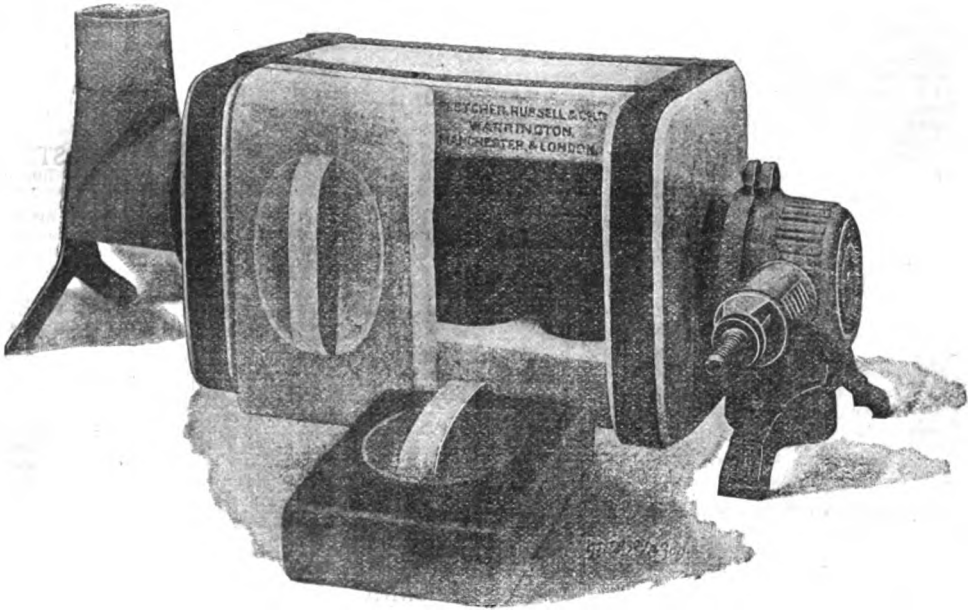
ginning from the end remote from the strontianite; the sulphur vapour, being slowly carried along the tube by the current of nitrogen, will gradually transform all the strontianite into sulphide. If pure strontium carbonate is used, the sulphide formed is not phosphorescent. The author finds traces of manganese in strontianite, which possibly affects the phosphorescence. He also draws attention to the fact that, if the sulphur vapour acts on the strontianite at a dull red heat, the sulphide is not phosphorescent. He makes a series of experiments on the influence of temperature on the formation of phosphorescent sulphide, and finds that there is a critical temperature above which sulphur vapour will always produce phosphorescent sulphide.

Combinations of Fatty Aldehydes with Mercuric Sulphate.—G. Denigès.—The results of treating ethyl and methyl aldehydes with mercuric sulphate are given. In the former case, the body $SO_4<^{Hg-O}_{Hg-O}>Hg.C_2H_4O$ is formed; in the second, mercurous sulphate is obtained.

Orthoxy-phenoxy-acetone.— C. Moureu.— Orthoxy-phenoxy-acetone, $C_6H_4<^{O-CH_2-CO-CH_3(1)}_{OH(2)}$, is produced when monochloracetone is heated on a water-bath with sodio-pyrocatechin. A description of its properties and of certain of its derivatives is given.

MISCELLANEOUS.

Laboratory Gas Furnace.—In the CHEMICAL NEWS for September 23rd last, on page 157, there appeared a description of a "New Laboratory Gas Furnace," illustrated with a woodcut. Messrs. Fletcher, Russell, and Co. send us the accompanying drawing, from which it is seen that the furnace previously illustrated is almost identical with one which Messrs. Fletcher, Russell, and Co. inform us has been made by them for the last fifteen or twenty years.



The World's Wheat Supply.—The wheat problem of the future as recently presented to the world by Sir William Crookes has met a whirlwind of criticism. But the more the subject is examined the more clearly it appears that Sir William is not an idle alarmist. Among the latest analyses of the subject is a paper in the *North American Review*, by John Hyde, Statistician of the Department of Agriculture, under the caption "America and the Wheat Problem." Mr. Hyde carefully reviews the production statistics, computes the area of available wheat lands, and arrives at the conclusion that in 1931, when the population of the United States is estimated to reach 130,000,000, it will be a serious task for this country to supply its own wheat consumption, assuming that the soil may maintain nearly its present supply of nitrogen. It is not probable, however, that the soil will retain its fertility unless, as Sir William Crookes has suggested, the laboratory comes to the assistance of the farmer. In the principal wheat-growing regions the soil is being robbed of its accumulated nitrogen with hardly a pretence of restoring it. The leguminous plants, such as clover and cowpeas, do not thrive upon these lands, and, even if they did, the resort to rotation would reduce their yield by limiting the wheat crop to every alternate year. In the older sections of the country the rotation with legumes is extensively practised, but clover utterly refuses to grow on some lands, so they are being either robbed of nitrogen or fertilised by the extremely expensive commercial preparations which cannot profitably be employed in wheat growing. There is one source of supply of nitrogen that may be made available, at least temporarily, without waiting for the development of the Crookes idea of extracting it directly from the atmosphere. That is the utilisation of the ammonia by-product from coke-making. Of course this supply is not equal to keeping pace with the wheat production of the world for any great period of time. Utilisation of the supply wasted in the form of sewage, to the detriment of the public health, is also to be considered as practicable and of great consequence, and the time has come for serious consideration of this branch of the subject, both from the economic and the sanitary standpoint. These two sources of nitrogen supply should be able to tide the world well over the period named by Sir William Crookes—a single generation. But it is by no means certain they will suffice for two generations if wheat consumption continues at anything like the present *per capita* consumption. This "if" is an important factor in the problem, since it is quite as probable that civilised man will change the proportion of wheat in his food supply as that he will be obliged to resort to laboratory extraction of nitrogen from the atmosphere. A taste may be cultivated for cowpea flour.—*Pittsburg Dispatch.*

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MEETINGS FOR THE WEEK.

TUESDAY, 21st.—Royal Institution, 3. "The Morphology of the Mollusca," by Prof. E. Ray Lankester, M.A., LL.D.
—— Society of Arts, 4.30. "The Commercial Development of Germany," by C. Rozenraad, F.S.S.
WEDNESDAY, 22nd.—Society of Arts, 8. "Electric Traction," by Philip Dawson.
THURSDAY, 23rd.—Royal Institution, 3. "English Playhouses in the Sixteenth, Seventeenth, and Eighteenth Centuries," by Willian Poel.
FRIDAY, 24th.—Royal Institution, 9. "Transparency and Opacity," by The Right Hon. Lord Rayleigh, M.A., D.C.L., LL.D., F.R.S.
—— Physical, 5. "On the Criterion for the Oscillatory Discharge of a Condenser," by Dr. Barton and Prof. Morton. "The Minor Variations of the Clark Cell," by A. P. Trotter.
SATURDAY, 25th.—Royal Institution, 3. "The Mechanical Properties of Bodies," by The Right Hon. Lord Rayleigh, F.R.S., &c.

TECHNOLOGICAL EXAMINATIONS, 1899.
CITY AND GUILDS OF LONDON INSTITUTE.

The Institute's Examinations in Technology will be held on April 26th, 29th, May 1st, 2nd, 3rd, 4th, 6th, 8th, 9th, 12th, 13th, June 3rd and 10th.

All applications from Local Secretaries for examination in Technology must be forwarded to the Institute on or before March 20th.

Only in exceptional cases, and by payment of an additional fee, can applications be received from Local Secretaries after that date.

Candidates in Technology not attending any registered class should apply at once to the Secretary of the nearest Local Centre.

Applications from any individual candidates for examination at the Offices of the Institute should be made not later than March 30th, addressed to the Examinations Department, City and Guilds of London Institute, Exhibition Road, London, S.W., and should be accompanied by a Postal Order for the amount of the fee—the Subject and Grade of Examination being clearly stated.

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Further particulars on application to the Director—

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THE CHEMICAL NEWS.

Vol. LXXIX., No. 2052.

THE BOILING-POINT OF LIQUID HYDROGEN AS DETERMINED BY A RHODIUM-PLATINUM RESISTANCE THERMOMETER.*

By JAMES DEWAR, LL.D., F.R.S.

The difficulties in liquefying hydrogen caused by the presence of air in the gas have been referred to (*Proc.*, 1898, xiv., 130), and later experiments have had for their object the removal of this fruitful source of trouble. This is by no means easy, as quantities amounting to only 1/1000 per cent accumulate in the solid state, and eventually choke the nozzle of the apparatus, necessitating the abandonment of the operation. Within the last week the author had succeeded in obtaining 250 c.c. of colourless liquid hydrogen, and this had been employed in a re-determination of the boiling-point. Earlier observations, made with a platinum resistance thermometer, had given −238° as the boiling-point, and a new thermometer, constructed from pure platinum from a different source, gave practically the same result. As this might be affected by some constant error, the determination was checked by employing a thermometer constructed from an alloy of rhodium and platinum, containing 10 per cent of the former. Alloys had been shown by Professor Fleming and the author to differ from pure metals in showing no sign of becoming perfect conductors at the absolute zero of temperature, and a study of the rhodium-platinum alloy had shown that the change in conductivity produced by cooling from 0° to the boiling-point of liquid air is regular, and may be represented by a straight line. As determined by the rhodium-platinum thermometer, the boiling-point of hydrogen was found to be −246°. Two ways of explaining the discrepancy between the two determinations suggested themselves. Pure platinum, although its resistance may be represented by a straight line almost down to the solidifying point of air, shows signs of a departure from regularity at about this point, and the curve may become asymptotic at lower temperatures. On the other hand, the resistance of the rhodium-platinum alloy diminishes less rapidly at these lower temperatures, and is much higher than that of pure platinum under similar conditions. It follows that its resistance-temperature curve, in all probability, deviates less from a straight line than is the case with platinum. Either cause would explain the differences observed, but the lower boiling-point, −246°, or 27° absolute, seemed to be the more probable, as it agreed very fairly with the value for the boiling-point calculated by the author from Wróblewski's results and that arrived at by Olszewski. As the use of other pure metals or alloys could not lead to more satisfactory results, the problem must be attacked in a different way by means of an "air" thermometer containing hydrogen under diminished pressure.

Addendum, March 17, 1889.—Since this paper was communicated the author has made a first attempt at determining the boiling-point by a constant volume hydrogen thermometer working under diminished pressure. The result is that this thermometer, which gave the boiling-point of oxygen as 90·5° absolute or −182·5°, gave for hydrogen 21° absolute or −252°. The three determinations that have been made are then as follows:—(1) pure platinum resistance thermometer 35° absolute; (2) rhodium-platinum resistance thermometer 27° absolute; (3) hydrogen thermometer 21° absolute. From this it appears that the boiling-point of hydrogen is really lower than was anticipated.

* A communication made to the Chemical Society, March 16th, 1899.

ON HYDROGEN PEROXIDE AS THE ACTIVE AGENT IN PRODUCING PICTURES ON A PHOTOGRAPHIC PLATE IN THE DARK.

By W. J. RUSSELL, Ph.D., V.P.R.S.

(Concluded from p. 125)

In former papers it has been shown that the active bodies, both metallic and organic, are able to act on a photographic plate even when thin layers of many different substances are interposed; for instance, if a thin sheet of gelatin be laid on a polished zinc plate it only very slightly modifies either the sharpness of the picture or the time required for its production. If the gelatin plate be thicker the action will still pass through, but the picture will be more indistinct, and the time necessary for its production longer. If a 2 per cent solution of hydrogen peroxide be poured into one of the small glass dishes, and a sheet of gelatin 0·0013 inch thick be placed over it ¼ inch above the liquid, a picture will be obtained in fifteen minutes. If the sheet of gelatin be 0·008 inch thick, then the exposure must be for one hour; and if the gelatin be 0·01 inch thick, an exposure of three hours is necessary. If a sheet of celluloid be substituted for the gelatin, and it be 0·005 inch thick, the action still passes through, but more slowly than through the gelatin, and the plate now requires one hour exposure to give a good picture. With a plate of celluloid of double the above thickness, the exposure must be four times as long; and if the thickness be 0·033 inch, the time of exposure has to be 30 hours. These determinations show well what happens in these cases, but are only good approximations, not standard results. In addition to gelatin and celluloid, guttapercha tissue, india-rubber tracing paper, collodion, albumin, gold beaters' skin, parchment, &c., also allow the action to take place through them, and the obvious question which presents itself is: If hydrogen peroxide be the body which gives rise to the action, how does it pass through these different bodies? Take the definite case of zinc, if a plate of this metal be rubbed with coarse sand-paper and placed in contact with a photographic plate, a clear and sharp picture of the scratches is obtained, and it might have been expected that when the action took place through even a very thin sheet of gelatin the picture of the scratches would have no longer been visible, or at least only indistinctly so, but experiment shows this is not the case. How then does the peroxide permeate the gelatin? Not by the ordinary process of diffusion, for hydrogen cannot diffuse through it, so that it must be by a process of dissolving, or very feebly combining with the medium, or with a constituent of it, and thus travelling through escape on the other side. That the action is of this nature seems rendered probable by the following experiments, which show, at least to some extent, what takes place.—

A 2 per cent solution of hydrogen peroxide was placed in a dish with a sheet of the thinnest gelatin about one hundredth of an inch thick; above it and on the gelatin a photographic plate was placed, and allowed to remain there for twenty minutes. No picture was formed. Immediately on removing this first plate from the gelatin, a second one was put in its place, and allowed to remain there also for twenty minutes. This plate gave a faint picture, the third one gave a darker picture, and the fourth one was still darker; but the fifth, sixth, and seventh plates were, as far as could be judged by the eye, of the same degree of darkness. Thus the amount of peroxide given off on the upper surface of the gelatin went on increasing for one hour and twenty minutes, and then the action became uniform. The same kind of action occurs if zinc be used in place of peroxide solution. If a thin sheet of gelatin be laid on a piece of zinc and allowed to remain there for a week, then, on placing above it a sensi-

* A Paper read before the Royal Society, March 2, 1899.

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tive plate, a picture will be produced in about one-third to one-fourth the time which would have been necessary if the previous exposure to the zinc had not taken place. Celluloid was found to act exactly in the same way as the gelatin. The plate, after the first half hour's exposure, gave no pictures, but a faint one after the second half hour; and it was not till after the fourth half hour that the action became constant. A thicker specimen, 0·011 inch thick, was also examined after intervals of two hours; it acted in the same way as the other specimens, but required ten and a half hours before the action became uniform. If drying oil or copal varnish be used in place of the peroxide of hydrogen solution, analogous results are obtained. This action explains how pictures can be obtained from invisible originals. If, for instance, a piece of white cardboard or paper is placed behind a copper stencil and is exposed to the vapour from peroxide of hydrogen solution, drying oil or copal varnish, &c., the exposed part of the paper becomes active, although not visibly affected, and on placing it on a sensitive plate, a picture of these parts is produced. Zinc acts in the same way, but only slowly. A zinc ornament, laid on a piece of Bristol board for eight months, charged the board only so far as to enable it to give a faint picture.

Gelatin can be substituted for the paper in these experiments, and can be charged and made to convey a clear picture to a sensitive plate. It is then evident that the action arising from zinc and other active bodies can, by an intermediate and inactive substance, be carried away and allowed to expend itself at another time and at another place.

With regard to the transmission of the action through gelatin, the water which it contains is probably the body which enables the peroxide to pass through. It can also be shown that it aids the transmission of the action through other inactive bodies; for instance, if Bristol board in its ordinary condition be placed on a polished piece of zinc, the action of the zinc only slowly passes through it, but if the board be damp the transmission takes place much more rapidly. The following comparative experiments illustrate this. Two similar pieces of Bristol board were taken, one was dried and then placed between a piece of perforated zinc and a sensitive plate and put under a bell jar with calcium chloride; the other piece of Bristol board was suspended over water until it was thoroughly damp and then placed between perforated zinc and a sensitive plate under a bell jar with a little water present. Both experiments were continued for twelve days, when it was found that with the dry board there was no picture produced, but with the damp one there was a good and dark one. If copal varnish be used in place of zinc, similar results are obtained, and if parchment be substituted for Bristol board the results are the same.

These experiments are, however, not conclusive, for it has been shown that with additional amount of water some of it finds its way to the zinc, and there induces the formation of more peroxide, which may account for the darker pictures. Even with the terpenes the additional amount of water may induce the additional formation of peroxide. This objection can, however, be obviated by cutting off the moisture in the damp medium from the active substance, or by using the aqueous solution of the peroxide as the origin of the action. In order to stop the aqueous vapour from either passing from the damp Bristol board or to it from the peroxide solution, a piece of tracing paper is interposed which allows the action to pass through it, but not any appreciable amount of aqueous vapour. On placing a sheet of tracing paper over a glass dish containing the peroxide solution and above it dry Bristol board with a photographic plate, in one and a half hours just an indication of a picture was produced, but when under the same conditions Bristol board which had been over water for nineteen hours was used, then a dark picture was formed. Again, similar experiments were made using a not highly glazed paper in place of the Bristol board, and the results were the same.

In place of tracing paper, celluloid was used and the dry Bristol board gave, under similar conditions, no picture, but the damp one a very distinct picture. In order to avoid having so much water present, plaster of Paris set by a little of the peroxide solution was used in place of the aqueous solution, and exactly similar results were obtained, so there is no doubt that hydrogen peroxide can readily pass through a porous body by the aid of water.

Alcohol acts in the same way as water, for when plaster of Paris wetted with peroxide solution was poured into a couple of similar dishes and allowed to set, and over one a piece of dry and over the other a piece of Bristol board moistened with alcohol were placed, and sensitive plates above them, after fifty minutes only a very faint picture was formed above the dry board, but a dark one over the wetted board.

Celluloid is, however, nearly as transparent to these actions as gelatin, and water in this case cannot be the transmitting medium, so that the question is whether there be any constituent of the celluloid which may act in a similar way to that of water in the gelatin. From the following experiments it seems that camphor can do so:—

Camphor itself, like water, is a perfectly non-active body. To obtain a thin non-porous layer of this body is difficult, but it is easy to prove that the emanations from hydrogen peroxide solutions, from zinc, copal, or other active bodies are readily absorbed by it, and readily pass through it. For instance, if a piece of camphor be placed about a quarter of an inch above a 2 per cent solution of hydrogen peroxide for seventeen hours and be then removed and placed on a sensitive plate for fifteen minutes, it gives a dark picture, and when a similar experiment is made, using drying oil in place of the peroxide solution, and the camphor be exposed to its action for three days and then brought in contact with the sensitive plate for one day, a dark picture is produced. This action can, however, be easily carried still further and proved to pass through even a thick layer of camphor. A piece 0·137 inch thick was placed about ½ inch above a 2 per cent solution of peroxide in a dish, for sixty-six hours, and a sensitive plate placed on the top of it; on treating this photographic plate with the developing solution it was found that a considerable amount of action had occurred. Thus the camphor which is a principal constituent of celluloid may enable hydrogen peroxide to pass through it.

That guttapercha and pure india-rubber should allow the action to pass through them is remarkable. The substance known as guttapercha tissue has a thickness of about 0·003 inch, and allows the action to pass readily through it; in fact, if even two thicknesses of this tissue be placed over the 2 per cent solution of the peroxide for seventeen hours, a dark picture is obtained. If the tissue be laid on a polished piece of perforated zinc and a sensitive plate above it, after remaining there for a fortnight a fairly good picture is obtained. If drying oil be used, the action will pass through the guttapercha in three days. With regard to this transmission of the action, although the chemical constitution of guttapercha is not well established, it is said to be a body related to camphor (Bernthsen, "Organic Chemistry," p. 509), and hence the action passes through it as it does through celluloid, and this is borne out by the fact that if a piece of guttapercha be placed for eighteen hours over the 2 per cent peroxide solution, and then placed for twenty minutes on a sensitive plate, it evidently has become active, for it then gives a good picture.

The above remarks apply also to india-rubber. The thinnest sheet that has been experimented with is 0·017 inch thick; this allowed the action to pass through it, but was too thick to give a picture, but, like the guttapercha, if placed over the peroxide solution it became active, and produced considerable action on a photographic plate.

With regard to other substances which allow the action to take place through them, the most interesting are true

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gold-beaters' skin and albumen. If Bristol board or paper be carefully painted on one side with white of egg and allowed to dry in the air, it forms a medium through which the peroxide can pass. Collodion also allows the action readily to pass through it. In all these cases the tetra-paper may be used to confirm the results obtained.

Then with regard to bodies which do not allow the action to pass through them. Paraffin is one of them. If paper be painted with melted paraffin and it be placed over a solution of the peroxide, no action passes through, neither is it able to absorb the peroxide like camphor and india-rubber and guttapercha. A piece of paraffin placed over the peroxide solution for twenty hours and then tested by placing it on a sensitive plate produced no action.

Gum arabic is a body which sometimes is very opaque, but this is simply a question of hydration, and is confirmatory of what has been said before with regard to the action of water. Some unglazed paper was painted on one side with two coats of good gum arabic, and some of it was dried at 55° for some days, and another portion of it was *air*-dried only for some hours, and both were put over drying oil for three days. The dried paper gave only a very faint picture, but the more moist one a very dark picture.

When experimenting some time ago on the general nature of these reactions, polished zinc was placed below some inactive liquids to test whether any action took place through them. The small glass dishes were used, and a disc of bright zinc laid inside, and the liquid to be tested poured upon it; then the photographic plate was placed on the top of the dish. After remaining there for three or four days the plate was generally found acted on as if the zinc had been able to exert its influence upon it. Lately these experiments have been repeated and extended, and, as indicating the extreme delicacy of the reaction with the photographic plates, are of interest. The form of experiment was the same as described above, and the liquids used were alcohol, ether, ethyl acetate, chloroform, benzene, petroleum spirit. All these liquids were purified, so that when placed in the dish with the sensitive plate above them no action after a week's exposure took place. However, when a zinc disc was introduced below the inactive liquids the photographic plate was generally acted on, but with the benzene and petroleum spirit sometimes no action occurred. These rather singular results were next tested in another way. Portions of these inactive liquids were put into stoppered bottles with polished strips of zinc foil, and allowed to remain there for a week, and it was then found that the liquid had become active, for on testing it by putting it into a dish with a photographic plate above it, a dark picture was formed, so that the action of the zinc was to make the whole of the liquid active. Magnesium, cadmium, aluminium, fusible metal, and bismuth, all produced effects similar to those obtained with the zinc, but nickel, lead, tin, &c., produced no such effects. Further it was proved that a very small amount of peroxide rendered alcohol, for instance, very active; 0·1 c.c. of a 2 per cent solution of the peroxide added to 10 c.c. of alcohol gave it the power of acting on a sensitive plate ½ inch above its surface, so as to produce in a few hours a dark picture. The still more careful purification of these liquids, and especially the exclusion of moisture, was undertaken, and in every case it was found when all moisture was excluded that the zinc had no longer the power, when below a liquid, of acting on a photographic plate. Specimens of alcohol, ether, and chloroform were prepared, and these when placed in a dish with zinc at the bottom of it (standing over sulphuric acid) allowed no action to pass through them, and when treated for a week or more with bright zinc in a bottle, still retained their perfect inactivity. To a sample of the alcohol which in a dish with zinc allowed no action on the sensitive plate above to occur, a trace of water was added, as much as adhered to the end of a thin glass rod, and now with the same length of exposure a dark picture was formed. From these experiments, as well as those previously mentioned, it appears that this action on the photographic plate is one of extreme delicacy.

The action of water alone on zinc is interesting, and appears to confirm the view that hydrogen peroxide is the active agent in all these reactions. It has already been shown that although bright zinc is active, dull zinc is inactive. However, if a piece of bright zinc be placed in water and remains there for twenty-four hours or so, it, of course, oxidises, white spots or lines appear, and, in fact, in time the whole surface would become covered with oxide. Now the oxide thus formed is strongly active. Take the plate out of the water, let it dry, place it in contact with a photographic plate, and a strong picture of the spots of oxide is obtained. No doubt peroxide of hydrogen is formed, and remains entangled in this porous oxide; in fact it is difficult entirely to remove it. The plate, with this oxide on it, may be dried at ordinary temperatures and exposed to the air for a day or two, and the oxide is still active, or it may be dried over calcium chloride or even exposed to a vacuum for some time, and it is still active, but if heated to 55° for seventeen hours then its activity is gone and a picture the reverse of the former one is obtained; that is, the oxide is now quite inactive, but the metal itself is very slightly active. Oxides of zinc, cadmium, and magnesium, if wetted with peroxide of hydrogen solution, act in the same way and retain their activity with great pertinacity.

From the foregoing experiments it is then concluded that hydrogen peroxide is the agent which directly or indirectly causes the changes in the photographic plate.

This investigation has been carried on in the Davy-Faraday laboratory, and I would again tender my best thanks to the managers of the Royal Institution for allowing me to work there. My thanks are also due to Mr. O. F. Block, who has most efficiently helped in carrying on the above experiments.

THE ESTIMATION OF POTASH.

By E. WIGHTMAN BELL, F.C.S.

Of the various methods which have been advanced for the estimation of potash, the processes which are undoubtedly still considered the most reliable are those in which precipitation is finally made as the double chloride of platinum and potassium.

The majority of the more trustworthy processes involve the elimination of phosphoric and sulphuric acids, and the earthy and metallic bases, accomplished as a rule by a not inconsiderable number of precipitations, washings, and evaporations, tedious in themselves, and accompanied by a possibility of loss of potassium either by occlusion or as the result of imperfect washings.

The following process, which the author has used for some time, not only considerably reduces the time required for a determination, but also yields a precipitate of greater purity than is usually obtained. A chemical friend, to whom the process was communicated, has, after trial in the laboratory of a large manure-works, reported very favourably thereon.

In the case of *manures*, 5 or 10 grms. of the sample are well boiled with about 150 c.c. of water, with or without the addition of a little hydrochloric acid. Ammonia is now added in sufficient quantity to produce a slight alkalinity; then, *without filtering*, a considerable excess of barium carbonate (usually about double the weight of manure taken) is added, and the boiling continued for half an hour. The mixture is now filtered, the precipitate washed, and filtrate and washings made up to 500 c.c.

Fifty c.c. to 100 c.c. of the solution are then evaporated to dryness with the addition of a small quantity of ammonium oxalate, gently ignited, treated with hot water, and

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filtered, the filtrate evaporated with hydrochloric acid and platinum chloride, and finished in the usual way.

Test analyses on mixtures of potash with superphosphate, bone, ammonium sulphate, sodium nitrate, &c., give results as under:—

Potash taken ..	0·1012	0·0500	0·2000	0·4250
„ found ..	0·1006	0·0498	0·2010	0·4230

In the case of *soils*, either the hydrochloric solution of the soil may be used (if K_2O soluble in HCl is required), and, after being rendered alkaline by means of ammonia, treated with barium carbonate, &c., as above, or the soil may be moistened with strong sulphuric acid, gently ignited, and the residue after boiling with water treated with barium carbonate, the boiling continued, filtered, and a portion of the filtrate then evaporated directly with hydrochloric acid and platinum chloride, without any previous addition of ammonium oxalate and ignition.

For the estimation of potash in *vegetable substances*, the organic matter should be moistened with sulphuric acid, ignited, and treated in a similar manner to soil.

A DELICATE REACTION OF HYDROGEN PEROXIDE.

By EDGAR S. BARRALET.

It is well known that solutions of hydrogen peroxide quickly oxidise the pale blue precipitate obtained by adding a solution of potassium ferrocyanide to a solution of a ferrous salt to "Prussian blue." Owing to the high colorific value of this pigment this reaction may be used as a delicate test for the presence of hydrogen peroxide,—in fact, for the detection of this compound in extremely minute quantities, since the oxidising agents, such as potassic bichromate, potassic permanganate, and calcium hypochlorite, cease to react at a far smaller degree of dilution.

Ten c.c. of hydrogen peroxide, 10 vols. = (3 to 3·2 per cent), were diluted to 100 c.c. with water; 10 c.c. of this diluted solution were now made again to 100 c.c. 20 c.c. of this solution diluted with water to 1 litre gives a solution of hydrogen peroxide containing 0·2 c.c. of hydrogen peroxide of 3 per cent strength, or approximately 1 part of H_2O_2 to 165,000 parts of water. Such a solution instantly intensifies the pale blue colour of ferrous ferrocyanide, 1 c.c. in 20 c.c. of the freshly precipitated compound being quite sufficient to make the reaction apparent. A similar addition of 1 c.c. of unboiled water has no effect. The ferrous ferrocyanide should either be freshly precipitated for each test or be kept in a bottle under a layer of petroleum.

ON THE COMPLEX SALTS OF PLATINUM OXALATES AND CHLORIDES.

By M. VÈZES.

I. Very little relation has yet been established by experiment between the two classes of saline compounds of platinum; on the one hand, the plato-oxalates, corresponding to the general formula $Pt(CO_2.CO_2)_2M_2$, in which M represents one atom of a monovalent metal, and, on the other hand, the chlorides, chloroplatinites $PtCl_4M_2$, and chloroplatinates $PtCl_6M_2$, which are the most frequently met with among the complex salts of platinum.

In particular the plato-oxalates appear to belong, by their constitution and properties, to the type of plato-salts, PtX_4M_2, to which the chloroplatinites belong; it also appears that they belong to this type through their method of preparation, and, further, that it should be possible to obtain them directly from the chloroplatinites by means of exchange reactions. Nevertheless the methods by which they are prepared up to the present do not depend on any of these simple relations; they all start from the more or less well-defined and difficultly obtained oxides. These methods, however, complicated from the theoretical point of view, are further difficult to carry out, and, as will be seen, not very applicable to the preparation of a notable quantity of the salts.

Doebereiner (*Pogg. Ann.*, xxviii., 180), who obtained the first oxalic derivative of platinum, prepared it by means of a badly defined and badly crystallised platinate of sodium, obtained by keeping a mixture of chloroplatinic acid and carbonate of sodium for a considerable time at a temperature of 100°; it appeared to correspond to the formula $Pt_3O_7Na_26H_2O$. This body dissolves, at the same time giving off carbonic acid gas, in a warm solution of oxalic acid, to which it imparts a very dark colour. The solution, when left to cool, becomes first green, then blue, and gives a deposit of fine reddish copper-coloured needles, which Dobereiner, without analysing them, took to be the platinous oxalate, C_2O_4Pt.

Souchay and Lenssen, in an extended research on the metallic oxalates (*Lieb. Ann. Chem.*, cv., 256), repeated Doebereiner's experiment, analysed the product formed, and assigned to it the formula $C_2O_4Pt+C_2O_4Na_2+4H_2O$, —that is to say, it is a double oxalate of platinum and sodium.

Söderbaum, who from 1885 to 1888 carried out a detailed research on the oxalic derivatives of platinum ("Studior öfver Plato-oxalylföremingar," 1888), finally prepared the same salt by also using Doebereiner's reaction, but he was much more careful in carrying it out. He prepared the platinate of sodium by the action of the chloroplatinate, $PtCl_6Na_2$, on an excess of melted soda, an operation which is difficult to perform, and dangerous to carry out on more than 15 grms. of material at one time.

The platinate obtained, mixed with carbonate of sodium, is then dissolved in a solution of oxalic acid heated on the water-bath: it is here important not to allow the temperature to rise above 70°, or else part of the platinum will be reduced to the metallic state. For the same reason it is far more convenient to work on small quantities of matter; Söderbaum only used 4 grms. of platinate for each operation. It can be seen from these details how complicated, inconvenient, and inapplicable this method of Doebereiner is, even when perfected by Söderbaum, for operations on a large scale.

The product thus obtained by Söderbaum is identical with the copper-red coloured needles analysed by Souchay and Lenssen; but this author, instead of taking it to be a double oxalate of platinum and sodium, considered it to be a complete salt, in fact a plato-oxalate, and represented by the formula $Pt(CO_2.CO_2)_2Na_2+4H_2O$. He justified this formula by preparing from this sodic salt the plato-oxalates of most of the other metals and a plato-oxalic acid $Pt(CO_2.CO_2)_2H_2+2H_2O$, from which all the preceding salts are derived.

These salts are all of a deep colour, analogous to that of the sodic salt just described; but most of them, when re-crystallised in a slightly alkaline solution, are changed into pale-looking crystals, totally different to the first crystals both in form and colour, having nevertheless almost exactly the same composition. Söderbaum, who was the first to observe this curious case of isomerism, and after him Werner (*Zeit. Organ. Chem.*, iii., 317), have both tried to explain this phenomenon by means of stereochemical considerations. It is more reasonable, however, to admit, as Werner has done in an hypothesis recently put forward (*Zeit. Anorg. Chem.*, 1896, xii., 50), that the plato-oxalates of the lightly coloured series are the only true plato-oxalates, and alone correspond to the formulæ given above; the salts of the dark coloured series being the products of the admixture of small quantities of unknown plato-salts with these plato-oxalates, corresponding to formulæ such as—

$Pt(CO_2.CO_2)2Cl_2M_2$, $Pt(CO_2.CO_2)_2Br_2M_2$, or $Pt(CO_2.CO_2)_2OM_2$.

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This hypothesis is rendered the more tenable by the already mentioned existence, among the salts of platinum, of other addition combinations of the same order,—for example, the so-called plati-cyanides of Hadow (*Chem. Soc.*, 1860, xiii., 106), which really correspond to the formula $5PtCy_4M_2+PtCy_4Cl_2M_2$; and also by the fact that the pale plato-oxalates pass easily to the state of their so-called copper-red isomers by careful oxidation with a little bromine or chlorine (Werner, *loc. cit*).

It is easily seen that none of the methods of preparation yet described are at all convenient; no one has made use of the relative compositions existing between the plato-oxalates and the other plato-salts, especially the chloroplatinites.

II. It is, however, possible to pass directly from the chloroplatinite of potassium to the corresponding plato-oxalate, from which all the other plato-oxalates can be produced; the change does not take place in an acid solution; even oxalic itself, in excess, is not able to displace the hydrochloric acid in these salts, but the reaction is, on the contrary, easily effected in a neutral solution.

To a warm concentrated solution of chloroplatinite of potassium we add an excess of neutral oxalate of potassium; we soon notice that the solution, of a deep red colour at first, takes a much lighter colour, and on cooling gives a deposit of straw-coloured prisms which act on polarised light. These characteristics suffice for distinguishing these crystals from the chloroplatinite which is of a deep red colour, from the chloroplatinate which is isotropic, and the oxalate of potassium which is colourless. Analysis shows, in fact, that these crystals are identical with the pale plato-oxalate prepared by Söderbaum.

	Calculated.		Found.				Söderbaum.
			I.	II.	III.	IV.	
Pt	194·8	40·16	—	—	40·45	—	40·35
2K	78·3	16·14	—	—	16·07	—	16·16
4C	48·0	9·89	—	—	—	10·36	—
8O	128·0	26·39	—	—	—	—	—
$2H_2O$	36·0	7·40	7·34	7·28	7·29	—	7·56

$Pt(CO_2.CO_2)_2K_2.2H_2O$
485·1 100·00

Thus, this salt is prepared by the regular reaction of double decomposition:—

$$PtCl_4K_2+2CO_2K.CO_2K.CO_2K=Pt(CO_2.CO_2)_2K_2+4KCl.$$

This reaction, which recalls the preparation of the plato-nitrite of potassium by means of the chloroplatinite and an excess of nitrite of potassium, thus constitutes the most simple method for the preparation of the pale plato-oxalate of potassium. It justifies Werner's opinion, quoted above, according to which the pale plato-oxalate should be the normal plato-salt corresponding to the chloroplatinate.

The inverse reaction of converting the plato-oxalate of potassium into the chloroplatinite is just as easy to perform, but the solution must be acid, as Söderbaum has shown (*loc. cit.*, p. 74). It suffices to add to the solution of plato-oxalate an excess of hydrochloric acid, to cause its colour to pass from yellow to red; after concentration, it deposits, on cooling, chloroplatinite of potassium:—

$$Pt(CO_2.CO_2)2K_2+4HCl=PtCl_4K_2+2CO_2H.CO_2H.$$

The plato-oxalate of potassium can be also prepared in a direct manner from chloroplatinate of potassium, by a reaction analogous to that made use of in preparing it from the chloroplatinite.

If we heat to boiling, a solution as concentrated as possible, of chloroplatinate of potassium, and add to it an excess of neutral oxalate of potassium (more than 3 molecules for each molecule of the salt), carbonic acid gas is given off at the expense of part of the oxalate, which reduces the plati-salt to the plato-salt, and after prolonged boiling the solution, on cooling, deposits pale yellow crystals of plato-oxalate of potassium. These crystals, which are from chloroplatinate, if the boiling has been sufficiently prolonged, are easy to distinguish from this salt, both by their paler colour and more particularly by their action on polarised light. The transformation of the chloroplatinate into the plato-oxalate may be represented by the following equation:—

$$PtCl_6K_2+3CO_2K.CO_2K=Pt(CO_2.CO_2)_2K_2+2CO_2+6KCl.$$

It provides a new method for the direct preparation of considerable quantities of plato-oxalate of potassium from the most common compounds of platinum.

As can easily be seen from the facts quoted above, the theoretical relations which unite the plato-oxalates to the complex chlorides of platinum give simple and practicable methods for the preparation of these salts; inversely these relations are justified by the existence of these methods of preparation.—*Bull. Soc. Chim.*, Series 3, vol. xix.-xx., No. 22.

LONDON WATER SUPPLY.

Report on the Composition and Quality of Daily Samples of the Water Supplied to London for the Month Ending February 28th, 1899.

By SIR WILLIAM CROOKES, F.R.S.,
and
PROFESSOR DEWAR, F.R.S.

To Major-General A. De Courcy Scott, R.E.,
Water Examiner, Metropolis Water Act, 1871.

London, March 10th, 1899.

Sir,—We submit herewith, at the request of the Directors, the results of our analyses of the 168 samples of water collected by us during the past month, at the several places and on the several days indicated, from the mains of the London Water Companies taking their supply from the Thames and Lea.

In Table I. we have recorded the analyses in detail of samples, one taken daily, from Feb. 1st to Feb. 28th inclusive. The purity of the water, in respect to organic matter, has been determined by the Oxygen and Combustion processes; and the results of our analyses by these methods are stated in Columns XIV. to XVIII.

We have recorded in Table II. the tint of the several samples of water, as determined by the colour-meter described in previous reports.

In Table III. we have recorded the oxygen required to oxidise the organic matter in all the samples submitted to analysis.

Of the 168 samples examined by us during the month, all were found to be clear, bright, and well filtered.

We have again to record an excess of rain. The rainfall at Oxford during the past month was 1·92 inches, the average fall for the past thirty years is 1·76 inches, giving an excess of 0·16 inch, and making the excess for the first two months of the year 0·85 inch, or 21·6 per cent on the average fall.

It is interesting to observe the effect of the rainfall on the number of microbes in the unfiltered Thames water. No rain fell on the 1st, 2nd, or 3rd, and the average number of microbes in the Thames at Hampton up to the 4th was 6510 per c.c.; it then rained every day until the 15th, during which time the average number of microbes, including the 16th, rose to 38,354 per c.c.; after the 15th no more rain fell, and the average number of microbes from then to the end of the month fell to 14,914 per c.c.

This large increase in the number of microbes in the river, due to rain, originates not merely from the washing of the surface of the land, but is also largely due to atmospheric microbes brought down by the rain. As far as our experiments go they are perfectly harmless.

Our bacteriological examinations of 239 samples have

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given the results recorded in the following table; we have also examined 37 other samples, from special wells, standpipes, &c., making a total of 276 samples in all:—

	Microbes per c.c.
New River, unfiltered (mean of 24 samples) ..	2995
New River, filtered (mean of 24 samples) ..	19
Thames, unfiltered (mean of 24 samples) ..	23280
Thames water, from the clear water wells of five Thames-derived supplies (mean of 119 samples)	54
Ditto ditto .. .. highest	620
Ditto ditto .. .. lowest	0
River Lea, unfiltered (mean of 24 samples) ..	7481
River Lea, from the East London Company's clear water well (mean of 24 samples) . ..	68

During the month the London waters, chemically and bacteriologically, have maintained their high character as an efficiently filtered river supply.

We are, Sir,
Your obedient Servants,
William Crookes.
James Dewar.

PROGRESS IN PHYSICAL CHEMISTRY.*

By THEODORE W. RICHARDS.

In these days of far-reaching specialisation the would-be speaker upon any subject is between a new Scylla and a new Charybdis. In order that his production should be comprehensible to those outside of the speciality it must almost inevitably be made boresome to those within the fold; but, on the other hand, that which is new to the specialist in his own topic is apt to be quite too new to the layman. Either popularising or specialising is likely to wreck the speaker's purpose by inducing at least a part of his audience to slumber, and this danger is especially imminent after dinner on a hot day which has been filled with mental effort. In this brief address, which Professor Smith has entrusted to my care, I shall probably run foul of both obstructions; but this irregular course will have the great concomitant advantage of permitting each class of hearers to obtain a few minutes of much needed repose.

We are rather accustomed to look upon physical chemistry as being a very modern invention, and in one sense we are not wrong in so doing. But after all, many of the fundamental generalisations of physical chemistry are by no means recent, and some of them are really old. Leaving out of account the probable discoveries in the subject made by Adam and Eve in the Garden of Eden, it is certain that the philosophers and alchemists were as much interested in those phenomena which lie on the border-line between physics and chemistry as in those which were purely physical or chemical. Indeed, the sharp line between the two subjects, drawn with so much emphasis twenty or thirty years ago, did not then exist. It is interesting to note that this sharp line is now rapidly being erased; we are realising more and more that the laws which govern one class of phenomena are applicable also to the other. Thus the cosmic working of the mind of man swings back and forth; will it ever come to rest upon the absolute truth?

In the middle of the seventeenth century, while this country was in an infantile condition, and Harvard College was little more than embryonic, Robert Boyle discovered his law relating to the contraction of gases under pressure—one of our most fundamental conceptions to-day. Lavoisier, before his tragic death in the Reign of Terror, forced upon a somewhat reluctant world the idea of the conservation of mass—an idea which perhaps had been assumed by some before—and in so doing laid a corner-stone of the great structure which was to follow. Only a few years later, Dalton, Avogadro, Ampère, Gay-Lussac, Dulong and Petit, Davy and Faraday, that prince of pioneers, with others less famous, made great additions to the world's thought in a physico-chemical direction. As far back as our forties Julius Robert Mayer and Helmholtz had acquired a clear grasp of the conservation of energy, while the other great law of energy had been partially realised by Sadi-Carnot two decades before. Hittorf's classical research on electrolytic conductivity, and Wilhelmy's epoch-making study of the speed of a reaction, a research upon the lines laid down by Wenzel and Berthollet so much earlier, took place over forty years ago. Only a decade later Guldberg and Waage laid down, in unequivocal and comprehensive terms, the fundamental law of mass-action, which is the basis of Wenzel's, Berthollet's, and Wilhelmy's observations, as well as of the progress and equilibrium of every other chemical change.

Why, then, with these foundations laid so far in the past, are we inclined to call physical chemistry a brand-new structure?

We all know that a part at least of the retarded development was due to the difficulty of dealing with solutions, which seemed anomalous in so many ways. Van't Hoff, by showing that a substance in solution followed many of the laws which would govern it in the aëriform state, and Arrhenius, by explaining in a simple way the differences between solutions conducting electricity and those which are non-conductors, cleared the track of these obstructions; hence for the last ten years the pace has been rapid. But it seems to me that there is another reason for the tardiness of the recognition of the importance of physical chemistry to be found in an unfortunate tendency observable sometimes in both chemists and physicists, a tendency which I am afraid we must call prejudice. Not only have untenable theories been held long after their time, but whole fields of study have been neglected by most chemists and physicists, because they lie on the border-line between the two sciences.

The average physicist only half realised that one of the most important relations of his great new force, electricity, is chemical, while the chemist does not always realise, even to this day, that Wheatstone's bridge and the telephone are chemical tools just as legitimate as, and no more "physical" than the thermometer, or the time-honoured balance, which extricated his predecessors from so hopeless a slough a hundred years ago. The day is fast approaching, however, when both chemist and physicist will welcome every mode of acquiring more light upon the absorbing topic which engages them in common—the study of the ultimate laws and structures of the universe.

It is a pleasure to think that one of the foremost of the brilliant men who have joined in advancing this wished-for end—this union of the resources of physics and chemistry to a common purpose—since the last meeting of the American Association has had its services recognised and his opportunity enlarged by his own University of Leipzig. Wilhelm Ostwald's new laboratory for physico-chemical research is the second important university building for this purpose which has been erected in Germany, the first having been built at Göttingen for the brilliant Walther Nernst; and the fact that Ostwald should at last have obtained a material outfit worthy of his unusual mental equipment is welcomed with enthusiasm by his many warm friends. We all know what a profound effect Ostwald's surprising book, his timely *Zeitschrift*, and in general his broad and progressive point of view, have had upon the development of both chemistry and physics, and it has been a matter of some surprise to many that so great an influence should have emanated from a laboratory so insignificant as the old Zweitem Laboratorium, so called. The new building,

* Address before Section C (Chemistry) of the American Association for the Advancement of Science, August, 1898.

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although no very large, is in many respects a model; the architect and director of any kind of scientific workshop could not fail to obtain valuable hints from the detailed statement of it contained in the recently published appendix to the *Zeitschrift für Physikalische Chemie*. What a pity that America should allow Germany to outstrip us so far in devotion to the ideals of pure science! How long will it be before we build laboratories especially for physical chemistry, or even in many colleges allot a considerable share of old buildings to this end? And yet this physical chemistry now comprehends all of the field of theoretical chemistry, except a certain kind of reasoning concerned with the structure of organic substances, and the purely chemical part of the mysterious classification called the periodic system of the elements.

Very few of the processes of nature are simple in their proximate causes or their outward manifestations, however simple the grand underlying principles may be in their ultimate essence. The old maxim, by which theories were so often consciously or unconsciously judged, "Our theory is so simple that it must be true," is a dangerous guide. Geber's old notion that the whole world consists of sulphur and mercury, and the topsy-turvy delusion of phlogiston, relied largely on this maxim for support, and it behoves us to avoid similar mistakes. When the ancient idea of luck had been eliminated from scientific reasonings mankind admitted that every phenomenon is a function of its controlling causes; but that all the mathematical relations should be capable of solution, although to be sure only with the aid of the potent modern methods, is a new conception. In the old days problems in chemistry which could not be solved by simple arithmetic, or at best by elementary algebra, were considered incapable of quantitative solution; now, the higher mathematics is a facile tool in the hands of many an eager chemist. Even that mystery of mysteries, the smallness of the yield in the preparation of organic substances, has a flood of light shed upon it by the phase-rule and the mass-law!

No one who is familiar with the facts can doubt that the mathematical point of view will prove in the future more and more useful to chemists, as well as to the new physical botanists and zoologists, who are bringing it to bear on their transcendently recondite problems. These last-named investigators will follow in the footsteps of chemists, as chemists have followed in the footsteps of physicists.

The advance of the mathematical point of view in chemistry has brought with it an entirely new danger, as well as a new field of power. The accuracy of a result, of course, depends upon the accuracy of the foundation upon which the reasoning rests; and accurate mathematical processes may lead to wholly erroneous conclusions if they are based upon incomplete data. In chemistry this cause of error is especially prominent, because of the great complexity of most of the phenomena and the fact that they are often modified by subordinate influences. For this reason a physicist, used to simple phenomena and less complex effects, is especially apt, when he deals with problems allied to chemistry, to erect a large superstructure of mathematical reasoning possessing the semblance of reality upon a paper foundation, and be drearily awakened some fine day by the collapse of his air castle. The only mode of guarding against this subtle cause of disaster is to bring as much skill into every step of the experimentation as into the pure reasoning based upon the supposed facts. Here the physicist is seriously hampered by his lack of knowledge of chemistry, as well as by his usual repugnance to dealing with glass vessels and liquids; while on the other hand, the chemist is equally hampered by his inbred dislike of brass instruments and his imperfect acquaintance with the manipulation of his new sensitive tools.

In short, one must be an accomplished chemist, physicist, and mathematician in order to attain the highest results in modern theoretical chemistry, and the number of men who have the time or ability to acquire this threefold education can never be large. All honour to van 't Hoff, Ostwald, Nernst, and the others who come nearest the high ideal! While it is true, however, that few men can hope to attain the highest, it does not follow that the rest of us cannot be of great use. Each man can be of value in his own particular sphere; it is only necessary that he should work faithfully with a single eye to the truth, that he should be as free as possible from prejudice, and that his published work should be as accurate as he can make it. A well-conducted organic synthesis, a few carefully determined solubilities, will in the end be more valuable to the progress of science than a false generalisation, no matter how ingenious the latter may be. But how great is the responsibility of the collector of facts! for if his observations are false his work is of less value even than of the false theorist; it has not even ingenuity in its favour, and is worse than useless. Ostwald has more than once pointed to the responsibility attending publication, and we should all do well to heed his warning.

A comprehensive design which I had once harboured of giving you a *résumé* of the year's work in physico-chemical research throughout the world has been relinquished because of the great number of small papers which could not be treated satisfactorily in the brief space of an evening's talk. The subject of stoichiometry, in Ostwald's rather comprehensive interpretation of this word, has received this year the attention usually accorded to it. Solutions have still occupied many able men, without having by any means had their possibilities exhausted. Van 't Hoff's admirable little book upon double salts has already begun to exercise an effect upon the chemical world which the scattered and less illuminating papers of his students could not have been expected to exercise. Dr. Gibbs's interesting Address upon this important topic will undoubtedly excite further study on the whole question of the so-called "molecular compounds," which are so little understood and so hard to reconcile with our only partially satisfactory ideas of quantivalence. The far-reaching subject of chemical equilibrium is receiving more and more attention every year. There has been great activity in the fascinating field of electro-chemistry, and it is pleasing to see that some of the fundamental notions of this new science are coming to be recognised by the analyst and the technical chemist. Not least among the startling events of the year had been the supposed discovery of a number of new elements, crypton, neon, metargon, coronium, and etherion; if these really exist, we have here a series of brilliant chemical discoveries made solely by means of physical instruments and operations.

The most important of these interesting investigations are undoubtedly as well known to you as to your speaker, for in this day the sources of information are equally open to all; hence it would be a work of supererogation for me to discourse upon them in detail, even if there were time to do so. I prefer, therefore, to call your attention to some unpublished work with which you can hardly be so familiar; I mean the physico-chemical problems which have enlivened the last winter's laboratory work at Harvard. Since these covered a somewhat extensive field, their exposition may serve the double purpose of illustration and information. It is a pleasure to state that most of these researches would not have been thought of without the inspiring example and precept of the great men of whom I have spoken. The host of interesting investigations thus prompted in all civilised lands afford the best possible proof of the value of the modern physico-chemical hypotheses.

Dr. Gordon, the Harvard assistant in physical chemistry, has finished a very interesting series of measurements of the potentials of galvanic cells composed of metallic plates immersed in fused salts at high temperatures. After overcoming experimental difficulties too numerous to mention, he succeeded in obtaining constant values

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which agree remarkably with Nernst's formula, and throw interesting light on the degree of dissociation existing in fused salts.

Mr. Edward Collins has nearly finished an elaborate attempt to verify Faraday's law with rigid exactness—an attempt which has met with greater success than any previous one.

Mr. G. N. Lewis made a series of careful measurements of the change of the potential of numerous reversible electrodes with the temperature, as well as a comprehensive revision of Meyer's inaccurate work on concentration cells involving amalgams of different strengths. In the thermodynamic discussion of the results Mr. Lewis arrived at some very interesting conclusions concerning strong as well as weak solutions of metal in mercury, and extended his experiment and mathematical analysis to the consideration of the potential of the unamalgamated metal in a solution of one of its salts. It is needless to say that this question is one of wide significance, but lack of time prevents my doing more than call attention to it now. Mr. Lewis's preliminary paper will appear early in the fall.

Mr. F. R. Fraprie spent much time in studying the eccentricities of inversion temperatures and transition intervals exhibited by the double sulphates of potassium and manganese. This problem proved to be far more complex and interesting than the similar case involving magnesium instead of manganese—a case which has been so carefully investigated under van't Hoff's supervision. While Mr. Fraprie was not able to push the matter to completion, he obtained data enough to enable one to plot many of the most essential curves and to draw a mental sketch of the situation. It is hoped that this work may be continued during the present year.

Mr. Faber, in the course of a research having a more practical end as its chief aim, made a series of determinations of the solubilities of argentic halides in solutions of sodic thiosulphate, and obtained data which may be of use in determining the mechanism of this reaction. Messrs. Harrington and Henderson made a few interesting observations on some cases in which the dissolving of a solid in a solution caused a lowering instead of a rise in the boiling-point, and Mr. Churchill made a careful determination of the melting-point of crystallised Glauber's salt. The aim of this last labour was to secure a new fixed point for the standardising of thermometers, and we succeeded in showing that the point was as easily obtained and as constant at 32·484° as could be desired. This means of verifying thermometers will be a great boon to those who have not a standard instrument at hand. The paper will appear in the *Zeitschrift für Physikalische Chemie* and in the *American Journal of Science*.

Besides these varied researches, a protracted study of the causes of the occlusion and the unequal release of gases by the oxides of metals formed from the nitrates, occupied most of my spare time. It became evident that the excess of oxygen usually present in such material has a tendency to work its way out by a process of dissociation and re-combination which reminds one of the old-fashioned explanation of electrolysis. The nitrogen, not being able to escape in this fashion, is retained. This paper has just appeared in the *Proceedings of the American Academy*.

In addition to these, several other researches were also in progress, which, although they belong strictly to the domain of inorganic chemistry, would never have been undertaken but for the theoretical interests involved. Prominent among these were the revisions of the atomic weights of cobalt, nickel, uranium, strontium, and calcium, undertaken by Dr. Cushman, Messrs. Baxter and Merigold, and myself.

Of course, it sometimes happens that physico-chemical problems involving the use of complicated apparatus may be more readily solved in a physical than in a chemical laboratory, and in any case the co-operation of these two departments is highly advisable. I am happy to say that Dr. Duane and others have been conducting such chemico-physical investigations at the Jefferson Physical Laboratory of Harvard College, but of these I have no authority to speak.

When one has been discussing the past and present progress of any subject, it is natural that the mind should turn to the future also. What fields are likely to prove the most fruitful in the years to come? What researches will probably best advance the interests of science, and, therefore, of the life of man? Prophecy is always an uncertain business; but if one recognises the uncertainty it has few dangers, and becomes at least amusing. In this case, however, it presents few difficulties.

The whole field of physical chemistry is so fruitful when treated by modern methods that one can hardly single out any section as especially unpromising. Almost every subject is worthy of research; a more important question is the *spirit* in which the research is to be undertaken.

There have always been two parties as regards any question brought forward by mankind for discussion—the conservative party and the radical party. The former has a tendency to cling to old ideas simply because they are old, and the latter has a tendency to adopt new ideas simply because they are new. It seems to me that neither of these tendencies is legitimate. One should seek new points of view continually, but he should hold to that which is good until something is proposed which seems to him better. In every case he should weigh the respective arguments for and against the new point of view with a mind as free as possible from prejudice, and with a single eye to the truth. In short, the ideal investigator is the scientific independent, the chemical "mugwump." Is it too unreasonable to hope that the problems of the twentieth century will be dealt with in this thoughtful but untrammelled fashion?

We Americans rejoice in having on our side of the ocean the world-renowned names of several great men, of Wolcott and Willard Gibbs, of James Crafts, Edward Morley, the late Josiah Parsons Cooke, and others, who have combined chemistry with physics and mathematics; but, nevertheless, one must admit that America has not done as much as one could wish toward building up the fabric of modern physical chemistry. Although science is world-wide, and scientific men should be cosmopolitan, the existence of this Association proves that there is a patriotic side to the matter too. While welcoming the truth, wherever it is discovered, let us then do all we can to further its emanation from American laboratories and writing-desks.

PROCEEDINGS OF SOCIETIES.

CHEMICAL SOCIETY.

Ordinary Meeting, March 2nd, 1899.

Professor Dewar, F.R.S., President, in the Chair.

(Concluded from p. 125.)

39. *The Action of Metallic Thiocyanates on certain Substituted Carbamic and Oxamic Chlorides; and a New Method for the Production of Thiobiurets.* By Augustus Edward Dixon, M.D.

Acid chlorides containing the group COCl interact with metallic thiocyanates, in presence of suitable solvents, yielding the corresponding organic isothiocyanates; chlorine united with certain groups, other than carbonyl, is similarly exchangeable, but complete dechlorination is generally hard to effect. Experiments made with a view of ascertaining whether the halogen in substances generally acidic in character, or only that in direct union with a negative group, could thus be substituted, pointed to the latter as the determinant condition.

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By heating with mercuric thiocyanate in presence of cumene, the chlorides of disubstituted carbamic acids are converted into isothiocyanates of the form $NR_2{\cdot}CO{\cdot}NCS$; these substances are related to the thiobiurets and to thioallophanic acid in the same way as ordinary thiocarbimides to thiocarbamides and thiocarbamic acid respectively. They unite spontaneously with nitrogenous bases, affording substituted thiobiurets, and, with benzylic alcohol, forming the corresponding substituted thioallophanates, $NR_2{\cdot}CO{\cdot}NH{\cdot}CS{\cdot}OBz$.

These thiobiurets may be regarded as thiocarbamides containing the carbamyl or $NR_2{\cdot}CO$-group; if so, the rule formulated by the author with respect to desulphurisation of the thiocarbamides by alkaline lead tartrate (*Trans.*, 1893, lxiii., 318) holds good, the carbamyl group here playing the same part as an alkylic or allyric radicle. Thus the thiobiurets, $NR_2{\cdot}CO{\cdot}NH{\cdot}CS{\cdot}NHX$, can be desulphurised when X is an aromatic radicle, but not when it is aliphatic. Their behaviour as carbamylthiocarbamides (or thioureas) is further instanced by the production of thiohydantoin-like derivatives on treatment with chloracetic acid; the latter compounds are related to the biurets in the same way as the thiohydantoins to the thiocarbamides, and, in like manner, yield thioglycollic acid on hydrolysis.

The isothiocyanates could not be freed from the accompanying cumene by distillation either with steam or under diminished pressure; their solutions were used in preparing the following derivatives:—

1. *Diphenylcarbamylisothiocyanate*, $NPh_2{\cdot}CO{\cdot}NCS$, with aniline gives acc-*triphenylthiobiuret*,—

$$NPh_2{\cdot}CO{\cdot}NH{\cdot}CS{\cdot}NHPH,$$

crystallising in white needles which melt at 163—163·5°, and yield phenylthiocarbimide when heated with acetic anhydride. a-*Orthotolyl*-c-*diphenylthiobiuret*,—

$$NPh_2{\cdot}CO{\cdot}NH{\cdot}CS{\cdot}NHTo,$$

from orthotoluidine, occurs in fine white needles melting at 163·5—164°. When desulphurised by silver nitrate it affords the corresponding *biuret*, $NPh_2{\cdot}CO{\cdot}NH{\cdot}CO{\cdot}NH\,To$, melting at 132—133°. a-*Paratolyl* c-*diphenylthiobiuret* melts at 172—172·5°, and resembles generally the ortho-derivative. a-*Methyl*-c-*diphenylthiobiuret* melts at 170—171°; the *ethylic* homologue at 137—138°, and the corresponding *benzylic* derivative at 167—168°. c-*Diphenylthiobiuret*, $NPh_2{\cdot}CO{\cdot}NH{\cdot}CS{\cdot}NH_2$, is precipitated on mixing the calculated quantity of alcoholic ammonia with the isothiocyanate solution; it forms long yellow prisms melting at 183°, and when fused with chloracetic acid yields n-*diphenylcarbamylthiourantoin*,—

$$NPh_2{\cdot}CO{\cdot}N{:}C{<}\begin{matrix}S{-}CH_2\\ NH{\cdot}CO\end{matrix}{>}$$ (*Trans.*, 1897, lxxi., 638),

which is deposited from alcohol in tufts of flexible needles, melts at 184—185°, and is hydrolysed by potash, forming thioglycollic acid. a-*Benzylphenyl*-c-*diphenylthiobiuret*, $NPh_2{\cdot}CO{\cdot}NH{\cdot}CS{\cdot}NPhBz$, from benzylaniline, occurs in white needles, becoming electrical on friction, and melting at 137—138°. a *Diphenylcarbamyl*-β *phenylthiosemicarbaside*, $NPh_2{\cdot}CO{\cdot}NH{\cdot}CS{\cdot}NH{\cdot}NHPh$, melts at 152·5—153°. *Benzylic*-a-*diphenyl*-β-*thioallophanate*, from the isothiocyanate and benzylic alcohol, occurs in vitreous, apparently rhombic, prisms melting at 141—142°; attempts to form similar compounds with methylic, ethylic, and cinnamic alcohols failed.

2. *Methylphenylcarbamylisothiocyanate*,—

$$NMePh{\cdot}CO{\cdot}NCS,$$

with aniline, yields a-*Phenyl*-c-*methylphenylthiobiuret*, $NMePh{\cdot}CO{\cdot}NH{\cdot}CS{\cdot}NHPh$, in woolly masses of needles melting at 158—159°. a-*Orthotolyl*-c-*methylphenylthiobiuret* forms thick, vitreous prisms melting at 108°; the *paratolyl* derivative occurs in white glistening plates melting at 156—157°. ac-*Dimethylphenylthiobiuret* forms leafy crystals melting at 90—91°. c-*Methylphenylthiobiuret*, $NMePh{\cdot}CO{\cdot}NH{\cdot}CS{\cdot}NH_2$, crystallises in brilliant apparently clinorhombic, prisms melting at 166—167°; with chloracetic acid it yields n-*methylphenylcarbamylthiourantoin*,—

$$NMePh{\cdot}CO{\cdot}N{:}C{<}\begin{matrix}S{-}CH_2\\ NH{\cdot}CO\end{matrix}{>},$$

a yellowish crystalline powder melting at 199—200°, and giving thioglycollic acid on hydrolysis. a-*Methylphenylcarbamyl*-β-*phenylthiosemicarbaside* crystallises from alcohol in brilliant prisms, melting at 119—120°; no evidence was obtained of the production of a stereo-, or other, isomeride. *Benzylic* a-*Methylphenyl*-β-*thioallophanate*, $NMePh{\cdot}CO{\cdot}NH{\cdot}CS{\cdot}OBz$, forms vitreous rhombohedra melting at 90—91°.

3. *Ethylphenylcarbamylisothiocyanate*, $NEtPh{\cdot}CO{\cdot}NCS$, forms the following derivatives:—a-*Phenyl*-γ-*ethylphenylthiobiuret*, melting at 106—107°; the *orthotolyl* and *paratolyl* compounds, melting at 124—125° and 174° respectively. c-*Ethylphenylthiobiuret* occurs in large, greasy-looking flattened prisms melting at 147—148°, and yielding, with chloracetic acid, n-*Ethylphenylcarbamylthiourantoin*, melting at 184—185°. *Benzylic*-a-*ethylphenyl*-β-*thioallophanate* crystallises in colourless prisms melting at about 120°.

4. *Benzylphenylcarbamylisothiocyanate*,—

$$NPhBz{\cdot}CO{\cdot}NCS,$$

resembles its congeners in forming a yellowish solution which has no distinctive odour, and can be desulphurised in the cold by ammoniacal nitrate of silver, or by boiling with alkaline lead tartrate. a-*Phenyl*-c-*benzylphenylthiobiuret*, $NPhBz{\cdot}CO{\cdot}NH{\cdot}CS{\cdot}NHPh$, occurs in colourless prisms melting at about 103°; the corresponding a-*Orthotolyl* compound melts at 131—132°, and when desulphurised, in presence of ammonia, by silver nitrate, yields a *guanidine*, $NPhBz{\cdot}CO{\cdot}NH{\cdot}C(NH){\cdot}NHTo$, melting at 136—136·5°. a-*Methyl*-c-*benzylphenylthiobiuret* forms white prisms melting at 99—100°; the a-*ethyl* derivative melts at 67—68°. c-*Benzylphenylthiobiuret* crystallises from a mixture of chloroform and alcohol in lustrous rectangular prisms; it melts at 179—180°, and with chloracetic acid yields the compound,—

$$NPhBz{\cdot}CO{\cdot}N{:}C{<}\begin{matrix}S{-}CH_2\\ NH{\cdot}CO\end{matrix}{>},$$

a sandy crystalline powder, melting between 194° and 195°, and affording thioglycollic acid on hydrolysis by potash. *Benzylic* a-*benzylphenyl*-β-*thioallophanate* separates from hot alcohol in brilliant vitreous prisms melting at 133—134°.

5. *Oxanilylisothiocyanate*, $NHPh{\cdot}CO{\cdot}CO{\cdot}NCS$, is obtained from phenyloxamic (oxanilic) chloride and lead thiocyanate in presence of toluene; its solution, when mixed with aniline, yields a-*phenyloxamyl*-β-*phenylthiocarbamide*, $NHPh{\cdot}CO{\cdot}CO{\cdot}NH{\cdot}CS{\cdot}NHPh$: it melts at 172—173°, and slowly dissolves in hot potash, producing phenylthiourea.

40. "*A Reaction of some Phenolic Colouring Matters.*" By A. G. Perkin.

In a preliminary communication (*Proc.*, 1898, xiv., 56) it was shown that some phenolic colouring matters which dye mordanted fabrics decompose the alkaline acetates in presence of alcohol, forming mono-substituted salts. The present investigation indicates the general nature of this reaction in the case of colouring matters having hydroxyl radicles in relatively ortho-positions, although in the flavone groups some exceptions occur. In the following list of the salts prepared, those of calcium and barium have been formed by double decomposition from the alkali compounds. The colour and crystalline form are given only in the case of the potassium salt, and all were obtained crystalline unless otherwise stated.

Anthraquinone Group.—Potassium alizarine, $C_{14}H_7O_4K$, violet needles; sodium alizarine, $C_{14}H_7O_4Na$; barium alizarine, $(C_{14}H_7O_4)_2Ba$; calcium alizarine, $(C_{14}H_7O_4)_2Ca$, and potassium monobromalizarine, $C_{14}H_6BrO_4K$. Potassium anthragallol, $C_{14}H_7O_5K$, violet black needles;

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also $C_{14}H_7O_5Na$; $(C_{14}H_7O_5)_2Ba$ (amorphous), and $(C_{14}H_7O_5)_2Ca$ (amorphous). Potassium purpurine, $C_{14}H_7O_5K$, and sodium purpurine, $C_{14}H_7O_5Na$, red needles. Potassium anthrapurpurine, $C_{14}H_7O_5K$, red needles. Other colouring matters of this group behave similarly, but quinizarine and metahydroxyanthraquinone do not give the reaction.

Flavone Group.—Morin yields the orange-yellow compounds, $C_{15}H_9O_7K$; $C_{15}H_9O_7Na$; $(C_{15}H_9O_7)_2Mg$; $(C_{15}H_9O_7)_2Ba$; $C_{15}H_5Br_4O_7K$; $C_{15}H_4Br_4O_7K_2$ (amorphous), and quercetin, $C_{15}H_9O_7K$; $C_{15}H_9O_7Na$; $(C_{15}H_9O_7)_2Ba(?)$; $C_{15}H_7Br_2O_7K$, orange coloured. Rhamnetin and rhamnazin are peculiar, and give respectively the salts $C_{16}H_{12}O_7.C_{16}H_{11}O_7K$ and $C_{17}H_{14}O_7.C_{17}H_{13}O_7K$. Potassium rutin, $C_{27}H_{31}O_{16}K$; potassium violaquercitrin, $C_{27}H_{25}O_{15}K$; potassium myrticolorin, $C_{27}H_{27}O_{16}K$, and potassium xanthorhamnin, $C_{28}H_{36}O_{17}.C_{28}H_{35}O_{17}K(?)$, are yellow amorphous powders. Fisetin forms $C_{15}H_9O_6K$, yellow needles, and myricetin, $C_{15}H_{10}O_8$, and luteolin, $C_{15}H_{10}O_6$, behave similarly, the latter with production of very soluble salts. Apigenin, $C_{15}H_{10}O_5$, and chrysin, $C_{15}H_{10}O_4$, do not give the reaction.

In the *xanthone* group, gentisin and euxanthone do not yield salts in this manner, but galloflavin (Bohn and Graebe, *Ber.*, 1887, xx., 1329), a possible member, forms the salt, $C_{13}H_4O_9K_2$, described previously. Maclurin, $C_{13}H_{10}O_6$ (pentahydroxybenzophenone), gives a readily soluble compound, and alizarine yellow A (trihydroxybenzophenone) the salt $C_{13}H_9O_4K$. Cotoin and phloretin do not give the reaction.

Potassium and sodium hæmatein, $C_{16}H_{11}O_6K$, and $C_{16}H_{11}O_6Na$, are described, but compounds of brazilein, $C_{16}H_{12}O_5$, are too soluble for isolation. Santalin, $C_{15}H_{14}O_5$ (?), forms $C_{30}H_{27}O_{10}K$ (amorphous) and curcumin appears to form an analogous compound. From morin, quercetin, and alizarin, alkali salts are formed by boiling alcoholic potash, by carbonates, nitrites, succinates, lactates, benzoates, and salicylates in the presence of absolute alcohol, and by potassium acetate in the cold. Morin appears to form the compound $(C_{15}H_{10}O_7)_2.C_2O_4K_2$ with potassium oxalate. The salts of the anthraquinone group dissolve unchanged in boiling water; those of the flavone, xanthone, and benzophenone groups are decomposed, forming the colouring matter.

From potassium alizarine, $C_{14}H_7O_4K$, the ethers $C_{14}H_7O_3{\cdot}OMe$ and $C_{14}H_7O_3{\cdot}OEt$ are formed from the iodides at 230°. Ethylanthragallol, $C_{14}H_7O_4{\cdot}OEt$, was also obtained. These contain the alkyl group in the meta-position, have previously been prepared by Schunck and Marchlewski (*Trans.*, 1894, lxv., 185), and by Liebermann and Jellineck (*Ber.*, 1888, xxi., 1169), and indicate the position of the acidic hydroxyl.

Monomethyl purpurine, $C_{14}H_7O_4{\cdot}OMe$, evidently $[OH:OCH_3:OH=1:2:4]$, forms red needles melting at 228—230°. Ethers of quercetin were not isolated in this manner, in consequence of accompanying decomposition.

To account for the acidic nature of these colouring matters, a change in the quinonoid form is suggested, capable of existence only in the form of a salt. Such a constitution has previously been proposed (*Trans.*, 1896, lxix., 1439) to explain the acid compounds of the flavone group, and a comparison of the *acid* and *basic* properties of these colouring matters reveals important points of resemblance.

Potassium alizarine, $C_{14}H_7O_4K$, is converted by cold acetic anhydride into *monacetylalizarin*, $C_{14}H_7O_4Ac$, crystallising in orange-yellow needles which melt at 198—201°; when allowed to remain some weeks with the reagent, diacetylalizarine is produced. Potassium-morin in the cold forms *tetracetylmorin*, $C_{15}H_6O_7Ac_4$, which crystallises in colourless prismatic needles, melts at 142—145°, and subsequently passes into a very soluble derivative. Potassium quercetin, $C_{15}H_9O_7K$, similarly gives *triacetylquercetin*, $C_{15}H_7O_7Ac_3$, melting at 167—169°, and quercetin sulphate, $C_{15}H_{10}O_7,H_2SO_4$, a *tetracetyl* compound which forms colourless needles melting at 193—194°.

The salts of morin and quercetin (Hlasiwetz and Pfaundler, *Jahresb.*, 1864, 560), of quercitrin (Liebermann and Hamburger, *Ber.*, 1879, xii., 1179), of fisetin (Schmid, *Ber.*, 1886, xix., 1739), and curcumin (Jackson and Menke, *J. Amer. Soc.*, 1882, iv., 77) appear to have been mixtures, as their percentage composition, though coinciding with the older formulæ of these colouring matters, does not agree with that required by their correct molecular weight.

41. "*Note on the Optical Activity of Gallotannic Acid.*" By Otto Rosenheim, Ph.D., and Philip Schidrowitz, Ph.D.

In a recent communication (*Trans.*, 1898, lxxiii., 878), the authors stated that the optical activity of gallotannic acid was first observed by F. M. Flawitzky, and that Günther independently re-discovered it in 1895, Flawitzky's communication remaining unnoticed. During the course of an investigation on the formation of gallic acid from gallotannic acid by the action of moulds, one of the authors (R.) has found that the merit of having first discovered the optical activity of the substance undoubtedly belongs to Ph. van Tieghem, who in a paper on "Fermentation du Tannin," says:—"Je me suis assuré que le tannin dévie vers la droite le plan de polarisation de la lumière incidente," and (*Ann. des Sciences Nat.*, 1867, [5], viii., 210) gives the specific rotation of the acid as $[\alpha]_D$ 16° +38·1°. This communication seems to have been unknown to Schiff, who six years later (*Annalen*, 1873, clxx., 75) devised the accepted gallotannic acid formula, and directly alluded to the "inactivity" of this substance, quoting F. W. Krecke's observations (*Arch. Néerl.*, 1871, vi., 193). It is remarkable that the important optical properties of this substance have been thrice discovered independently, and that until quite recently these have not become generally known and are not mentioned in any of the best known text- or hand-books. The fact that van Tieghem did not mention his discovery in a report on the subject (*Comptes Rendus*, 1867, lxv., 109), and that his original communication appeared in a botanical journal more or less inaccessible to chemists, may account in part for this omission.

CORRESPONDENCE.

ABSTRACTS OF CHEMICAL PAPERS.

To the Editor of the Chemical News

Sir,—Professor Stokes's letter on Chemical Abstracts has indicated clearly the disadvantages of the duplication of abstracts; his suggestion of co-operation of English-speaking nations is one which will commend itself favourably to the consideration of all who are interested in the advance of chemical science.

The scheme is one of considerable magnitude, and the details will require most careful consideration: I would draw attention to the fact that a needless duplication of abstracts occurs among our English Journals, and a consideration of how to avoid this must take place concurrently with, if not previous to, any discussion of Professor Stokes's proposition.

To illustrate my point, I will take those abstracts which come most under my notice—those on Analytical Chemistry; not infrequently I find abstracts, not only in your Journal, and in the *Analyst* (which is, in my opinion, the place where we should look for analytical abstracts), but in the *Journal of the Chemical Society*, the *Journal of the Society of Chemical Industry*, and sometimes in the *Journal of the Institute of Brewing*. Seeing that the size of our Journals shows a progressive increase, I can-

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not but think that it would be a great advantage if the parent body, the Chemical Society, would call a conference of delegates from the various societies interested in chemistry (including naturally the Editors of the Journals) to consider the simplification of English abstracts, as well as the feasibility of the views put forward by Professor Stokes.—I am, &c.,

H. Droop Richmond.

Rodbourne, Claremont Road, St. Margarets, March 18, 1899.

NOTICES OF BOOKS.

The Microscopy of Drinking Water. By George Chandler Whipple. New York: John Wiley and Sons. London: Chapman and Hall, Ltd. 1899. Pp. xii.-300. 8vo., 19 plates.

The author, who is Biologist and Director of Mt. Prospect Laboratory connected with the Department of Water Supply, Brooklyn, New York, and who had experience as Biologist of the Water Works at Boston, Massachusetts, has prepared this handsome volume with a twofold purpose. As he writes in the Preface, "It is intended primarily to serve as a guide to the water analyst and the water-works engineer, describing the methods of microscopical examination, assisting in the identification of the common microscopic organisms found in drinking water, and interpreting the results in the light of environmental studies. Its second purpose is to stimulate a greater interest in the study of microscopic aquatic life and general limnology from the practical and economic standpoint."

The subjects treated of in Part I. embrace methods of microscopical examination, its object, the organisms occurring in water from various sources (rain-, river,- and pond-water, canals, &c.); the physical properties of water (limnology); the geographical distribution of microscopic organisms, their seasonal distribution, as well as their horizontal and vertical distribution; the peculiar odours in water supplies, and their causes; the storage of surface water and of ground water; and the growth of organisms in reservoirs and water-pipes. The illustrations have been drawn chiefly from biological researches made at American localities, but the methods of examination, and to a large extent the aquatic life described, will prove equally valuable to investigators in Great Britain.

Part II. is devoted to descriptions of the most common organisms found in water supplies. In order to bring the matter within the scope of a practical and elementary survey, the descriptions are limited to the genera, no attempt being made to describe species and varieties.

A feature of the volume is the nineteen plates, the drawings having been made from photo-micrographs of living specimens, though some have been reproduced from standard publications. The Appendices contain useful tables and formulæ, and a bibliography of 483 entries. There is a well-made Index to the volume. The typography and paper do credit to the publishers.

H. C. B.

Practical Work in Physics. For Use in Schools and Colleges. By W. B. Wollacombe, M.A. (Oxon), B.Sc. (Lond.), Fellow of the Royal Astronomical and Physical Societies of London; Senior Science Master in King Edward's High School, Birmingham. Part IV.—Magnetism and Electricity, Oxford: at the Clarendon Press. 1899.

This modest little book is the fourth of the series of Practical Physics for Schools and Colleges; the previous issues have already been noticed in our columns, and we are glad to see that this last is quite up to the standard of excellence that has marked the others. The author's experience as a science master of long standing has enabled him to arrange the matter in the way most suited to the purpose in view, and the experiments described, though complete, are clear and simple. The apparatus needed is not costly, and most of it can be made by the pupil himself—a matter of very considerable value, as it gives him a clearer idea of the forces with which he is working than can be obtained when using the highly finished apparatus of the instrument maker, while at the same time there is a great saving in expense. Of the multitude of books for use in schools this series is certainly one of the best, and we are glad to learn that so far it has been favourably received.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

Note.—All degrees of temperature are Centigrade unless otherwise expressed.

Comptes Rendus Hebdomadaires des Séances, de l'Académie des Sciences. Vol. cxxviii., No. 8, February 20, 1899.

Complex Oxides of the Rare Earths.—G. Wyrouboff and A. Verneuil.—Cerium possesses—in addition to the simple oxides, CeO, Ce_3O_4, and the peroxide obtained by the action of hydrogen peroxide on these oxides—the oxides Ce_3O_43CeO, and Ce_3O_4CeO; the first giving only non-condensed compounds, the second giving stable compounds only when CeO is replaced by one or other of the cerite or yttria earths. Ceroso-ceric oxide, whilst combining with lanthanum, didymium, and yttrium, forms complex oxides of the form Ce_3O_4MO, which polymerise with great facility and give two isomeric oxides, both condensed. In this state they form with acids, acid or neutral salts analogous to those of pure cerium. The discovery of these facts is of great importance in the separation of cerium from neighbouring metals. It follows that the methods used hitherto are perfectly irrational, and by a method shortly to be announced, depending on the above statements, cerium can be separated quantitatively, and consequently exactly estimated in the presence of any of the rare earths.

Action of Oxidising Agents on certain Amides.—Œschner de Coninck.—Not suitable for abstraction.

New Method of Preparation of Mixed Alcohol and Phenol Phosphoric Esters.—Albert Morel.—The author demonstrates the possibility of forming mixed phosphates by a method analogous to that for forming mixed carbonates, *i.e.*, by the reaction of alcoholates on triphenyl phosphate. A solution of $PO(OC_6H_5)_3$ in a mixture of absolute alcohol and anhydrous ether was treated successively with one, two, and three molecules of sodium ethylate dissolved in excess of absolute alcohol. The three products obtained were—

$$PO\begin{matrix}OC_2H_5\\(OC_6H_5)_2\end{matrix}, \quad PO\begin{matrix}(OC_2H_5)_2\\OC_6H_5\end{matrix}, \text{ and } PO\begin{matrix}(OC_2H_5)_2\\ONa\end{matrix}.$$

The triethyl phosphate was not obtained by this method, which is probably accounted for by the dissimilarity existing between one of the hydroxyls of phosphoric acid and the other two. Conversely, triethylphosphate, treated with water, gives the stable diethylphosphoric acid,—

$$PO\begin{matrix}OH\\(OC_2H_5)_2\end{matrix}.$$

Action of the Amyl Alcohol of Fermentation on its Sodium Derivative.—M. Guerbet.—The author has isolated three products of the reaction ensuing when amyl alcohol is warmed with sodium, viz., an alcohol, $C_{10}H_{22}O$; an acid, $C_{10}H_{20}O_2$; and isovaleric acid. The formation of these bodies may be expressed as follows:—(1). $C_5H_{11}NaO+2C_5H_{12}O=C_{10}H_{22}O+C_5H_9NaO_2+4H$: (2). $C_{10}H_{20}O+NaOH=C_{10}H_{19}NaO_2+4H$.

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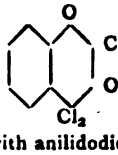
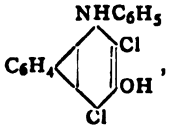
Liebig's Annalen der Chemie,
Vol. ccc., March 9, 1898.

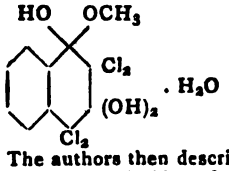
On 2.4-Tetrachloro-1.3-dicetotetrahydronaphthalene.—Th. Zincke and G. Egly.—To obtain the 1.3.2.4-(meta) derivatives,—



the authors started with anilidodichloronaphthol β,—



which they treated with chlorine. But since then naphtharesorcine, or 1.3-dioxynaphthalene, has been discovered, and this substance is found to be much better for the preparation of the *m*-diacetotetrachloride. Chlorine is passed through a solution of naphtharesorcine in ten parts of acetic acid until saturation. After twenty-four hours, this is evaporated down, and the residue treated with water and a little hydrochloric acid. The hydrate of the dicetachloride, $C_{10}H_4Cl_4O_2.3H_2O$, is then deposited in flattened needles, which are purified by crystallisation in warm benzene. The anhydrous dicetochloride crystallises in boiling benzene in prisms, generally arranged in groups or stars. If the hydrate of the dicetochloride is boiled with methanol in a flask fitted with a vertical condenser, and the excess of this latter then driven off by evaporation, a syrupy product remains which, when crystallised in hot benzene, forms needles fusible at 156°; it is the methylate, to which the constitution—



has been given. The authors then describe the action of Na_2CO_3 on the dicetatetrachloride, of Cl_2CaO on the *m*-dicetatetrachloride represented by the equation $C_{10}H_4Cl_4O_2 + ClOH = C_{10}H_5Cl_5O_2$, and of KOH on pentachloracetonic acid.

Carbonates of the Dioxybenzenes.—A. Einhorn.—Having observed that, when concentrating an alcoholic solution of carbonate of pyrocatechin by heat, this compound is converted into an oxethyl-derivative, the author turned his attention to the amines, and found that these, and especially the secondary amines, lead very easily to derivatives of the formula $C_6H_4<^{OCONRR'}_{OH}$. He then extended his researches to the carbonates of the other dioxybenzenes. A number of these, such as ethyl carbonate of pyrocatechin, amylcarbonate of pyrocatechin, phenylhydrazide, &c., and their properties are then described. To obtain carbonate of resorcine free from chlorine, it is necessary to react with 25 grms. of phosgene dissolved in toluene on 30 grms. of resorcine dissolved in 250 grms. of pyridine at 0° while constantly agitating. After half an hour, the whole is poured into water and the carbonate is precipitated; it is in the form of an amorphous powder, fusible at 190°, and has not yet been crystallised. The action of piperidine on this carbonate gives two products, the piperidide, $C_6H_4(OH)_m.O.CO.NC_5H_{10}$, which is soluble, and the dipiperidide, $C_6H_4(OCO.NC_5H_{10})^1_{.3}$, which is insoluble.

Reduction of Benzylamine-carbonic Acids.—A. Einhorn and J. Brantl.—The most interesting of these denitrated products is the *o*-oxymethylhexahydrobenzoic acid. It is without doubt formed by the splitting up of the cis-hexahydro-*o*-diethylbenzylaminecarbonic acid into diethylamine and hexahydrophthalide, $C_6H_{10}<^{CH_2}_{CO}>O$, and the subsequent hydratation of this latter, which is lactone.

Dimethylaniline-phthaloylic Acid.—H. Limpricht.—This acid, of which the formula is—

$$C_6H_4<^{CO—C_6H_4N(CH_3)_2}_{COOH},$$

is produced by the action of 40 grms. of $AlCl_3$ on a mixture of 45 grms. of phthalic anhydride, 37 grms. of dimethylaniline, and 200 grms. of bisulphide of carbon; the chloride of aluminium must be added a little at a time as it causes a rise of temperature. The residue, after boiling and distillation, is dissolved in dilute warm hydrochloric acid, the phthaloylic acid is deposited on cooling in the form of yellow crystals fusible at 205°, and soluble in alcohol, acetone, and benzene, slightly in ether, very slightly in CS_2, and not at all in water. When submitted to a prolonged reduction by NH_3 and zinc at about 80°, phthaloylic acid gives rise to a hydro-derivative—

$$C_6H_4<^{CH_2C_6H_4N(CH_3)_2}_{CO_2H}.$$

The Action of Chloride of Tetrazodiphenyl on Acetylacetic Acid and on the Phenylhydrazone of Benzylic Aldehyde.—E. Wedekind.—Twenty grms. of acetylacetic ether were saponified by 10 grms. of KHO with 345 c.c. of water. After cooling with ice, a solution of tetrazoic chloride (obtained from 28·5 grms. of benzidine) was added. The dark brown product was then washed with water, dried, and exhausted with boiling chloroform. By adding ligroïn to the concentrated chloroformic solution, the cyclocetone is separated in the form of a reddish brown amorphous powder, slightly soluble in the ordinary solvents, and soluble in H_2SO_4 with a green colour; by adding water it is re-precipitated unchanged. Sulphide of ammonium reduces cycloformazylcetone, giving a compound crystallising in boiling chloroform in brownish prisms melting at 145—148°. The action of phenylhydrazin gives a brown body melting at 180—185°, from which an orange compound is extracted by soda; the crystals are fusible at 197°, and dissolve in sulphuric acid, giving a crimson colour.

MEETINGS FOR THE WEEK.

WEDNESDAY, 29th.—Institution of Mining and Metallurgy, 6.30. Annual General Meeting.
— Chemical, 3. Anniversary Meeting. Election of Officers and Council. President's Address.

Chemist wanted for large Works in North of England. Preference given to one well up in Iron, Steel, and Fuel Analysis.—Apply, giving full particulars and salary required, to "Iron," Chemical News Office, 6 & 7, Creed Lane, Ludgate Hill, London, E.C.

Wanted, an Analytical Chemist for Mines in Central America.—Reply, Santa Francisca Gold Mines, Ltd., London and South Western Bank Buildings, Small Street, Bristol.

Wanted, an Analytical Chemist of exceptionally high and proved ability and accuracy, with good experience in testing Medicinal Chemicals, to take up the position of Chief Analyst at the Works of a leading London Firm of Manufacturing Chemists. A gentleman who has taken University Degrees preferred.—Address, stating age, qualifications, and experience, to "Analyst," care of Messrs. Markby, Stewart, and Co., Solicitors, 57, Coleman Street, London, E.C.

TO INVENTORS AND EXPERIMENTALISTS.

Laboratories specially fitted up for Experimental and Analytical work can be hired in Westminster at reasonable prices. Arrangements also made for placing inventions on the market.—Apply to L. W., Chemical News Office, 6 and 7, Creed Lane, Ludgate Hill, London, E.C.

Analytical Laboratory, fitted for Bacteriological Work, For Sale; in good position; low rent; no reasonable offer refused.—Apply, Baird and Tatlock, 14, Cross Street, Hatton Garden, E.C.

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THE CHEMICAL NEWS.

VOL. LXXIX., No. 2053.

ON THE ORDER OF APPEARANCE OF CHEMICAL SUBSTANCES AT DIFFERENT STELLAR TEMPERATURES.*

By Sir NORMAN LOCKYER, K.C.B., F.R.S.

In a paper on the "Chemistry of the Hottest Stars," in 1897 (*Roy. Soc. Proc.*, vol. lxi., p. 148), I stated the results so far arrived at concerning the order in which certain spectral lines appeared and others disappeared in stars arranged in a series of ascending temperatures. Since that paper was written many important advances have been made, so that I have been able in the meantime to considerably extend the research. Among these advances I may mention the following:—

1. With regard to the metals, my recent note on the enhanced lines in the spectrum of α Cygni (*Supra*, p. 320) enables us to deal with the lines observed at the highest temperature in the spectra of the following substances:—Fe, Mg, Ca, Sr, V, Ti, Ni, Mn, Cr, and Cu.

The temperature ranges of the enhanced lines of these metals have been investigated with the following results:—

TABLE I.

Metal.	Range of temperature (upward series).	Range of temperature (downward series).
Mg ..	α Ursæ Min. to γ Argus	α Eridani to Procyon.
Ca ..	α Tauri to γ Agrus	α Eridani to Arcturus.
Fe ..	α Tauri to ζ Tauri	β Persei to Arcturus.
Ti ..	α Tauri to ζ Tauri	β Persei to Arcturus.
Cu ..	α Ursæ Min. to α Cygni	β Persei to Procyon.
Mn ..	α Ursæ Min. to α Cygni	β Persei to Procyon.
Ni ..	α Ursæ Min. to α Cygni	β Persei to Procyon.
Cr ..	α Ursæ Min. to α Cygni	γ Lyræ to Procyon.
V ..	α Ursæ Min. to α Cygni	Sirius to Procyon.
Sr ..	α Tauri to α Cygni	Sirius to Arcturus.

I pointed out in the note referred to that the enhanced lines of the above substances seemed to account for almost all of the more marked lines in α Cygni. It is on this ground that I have investigated their behaviour in other stars before waiting for the results of the complete inquiry. Another reason has been that although in addition to the enhanced lines of the metals shown in the foregoing table, those of—

Ba, Cd, Mo, La, Sb, Pd, Ta, Rh, Er

and—

Yt, Ce, Wo, U, Zr, Pb, Co, Bi,

have already been investigated with lower dispersion, and a spark obtained with the use of a much less jar capacity, so far I have no certainty that any of these substances exist in the reversing layers of stars of intermediate temperature.

2. The temperature ranges of the arc lines of some of the metals have also been investigated, and the results are shown in the following table:—

TABLE II.

Metal.	Range of temperature (upward series).	Range of temperature (downward series).
Fe ..	α Tauri to α Cygni	α Canis Majoris to Arcturus.
Ca ..	α Tauri to α Ursæ Min.	α Canis Majoris to Arcturus.
Mn ..	α Tauri to α Ursæ Min.	α Canis Majoris to Arcturus.

* A Paper read before the Royal Society, February 23, 1899.

3. The new series of lines discovered by Professor Pickering, and described by him as representing a new form of hydrogen (*Astro. Phys. Journ.*, 1897, vol. v., p. 92), has been found in the spectra of ζ, ε, δ, and κ Orionis photographed at Kensington in 1892, and Mr. McClean has traced the lines in γ Argus.

We are therefore now in a better position to determine the relation of this new gas to other gases, both known and unknown, appearing in stars of nearly equal temperature.

4. In addition to the unknown lines at λλ 4089·2 and 4649·2, referred to in my last communication on this subject (*Roy. Soc. Proc.*, vol. lxii., p. 52), three other unknown lines occur in γ Argus.

As these most probably reveal still undiscovered gases, I include them in Table III., showing the limits of stellar temperature to which the various known and unknown lines, probably of gaseous origins, extend.

5. Mr. McClean has stated that certain of the oxygen lines (amongst which is the strong triplet at λλ 4070·1, 4072·4, and 4076·3) appear in the spectrum of β Crucis and other stars of nearly equal temperature. My own observations, so far as they have gone, tend to confirm this view, but other photographs and more laboratory work are needed to explain certain changes of intensity which have been observed. The lines attributed by Mr. McClean to oxygen have been noted between α Crucis and ζ Orionis in the upward series, and in stars at about the α Eridani stage of temperature in the downward series.

6. There is evidence that the strongest lines of nitrogen at λ 3995·2 and λ 4630·9 make their appearance in stars at about the temperature of α Crucis. These lines appear from Rigel to ζ Orionis in the upward series, and are present in stars at the α Eridani stage in the downward.

7. I pointed out many years ago (*Roy. Soc. Proc.*, vol. xxx., p. 461) that at high temperatures the flutings of carbon in the violet are replaced by a line at λ 4267·5. There is a line at this wave-length in the spectra of stars ranging in temperature from that of Rigel to ζ Orionis on the up side, and from α Eridani to β Persei on the down side, of the temperature curve.

There is no known line of gases or metals to which this line can be assigned. It is probable therefore that carbon exists in stars of the same temperature as that at which oxygen and nitrogen have been traced.

8. Two lines in the spectrum of silicium (λ 4128·5 and λ 4131·5) have been traced in stars between the temperatures of α Ursæ Min. and α Crucis in the upward series, and between those of α Eridani and Procyon in the downward.

The accompanying map shows the facts relating to stars as hot as, or hotter than, the sun, as we know them at present.

Description of Map.

The map is arranged on the following plan:—The temperature of the sun and Arcturus forms the lowest stage. The upper limit is defined by γ Argus, the hottest star so far known. On the left the stars named are those of increasing temperature; on the right those of decreasing temperature. Those on the same horizon represent equal mean temperature so far as the cleveite gas and enhanced lines help us to determine them. The blank spaces indicate that so far no star has been photographed in the spectrum of which the enhanced lines exactly match those on the opposite side.

The names of the various chemical substances included in the discussion are given at the top. I have retained the prefix "proto" to that condition of each metallic vapour which gives us the enhanced lines alone, and I have added it to that form of hydrogen seen only in the hottest stars.

The behaviour of the most typical line of each chemical substance is indicated by a double line looped at the top at its highest range. The length and varying thickness of the lines in stars on both sides of the temperature

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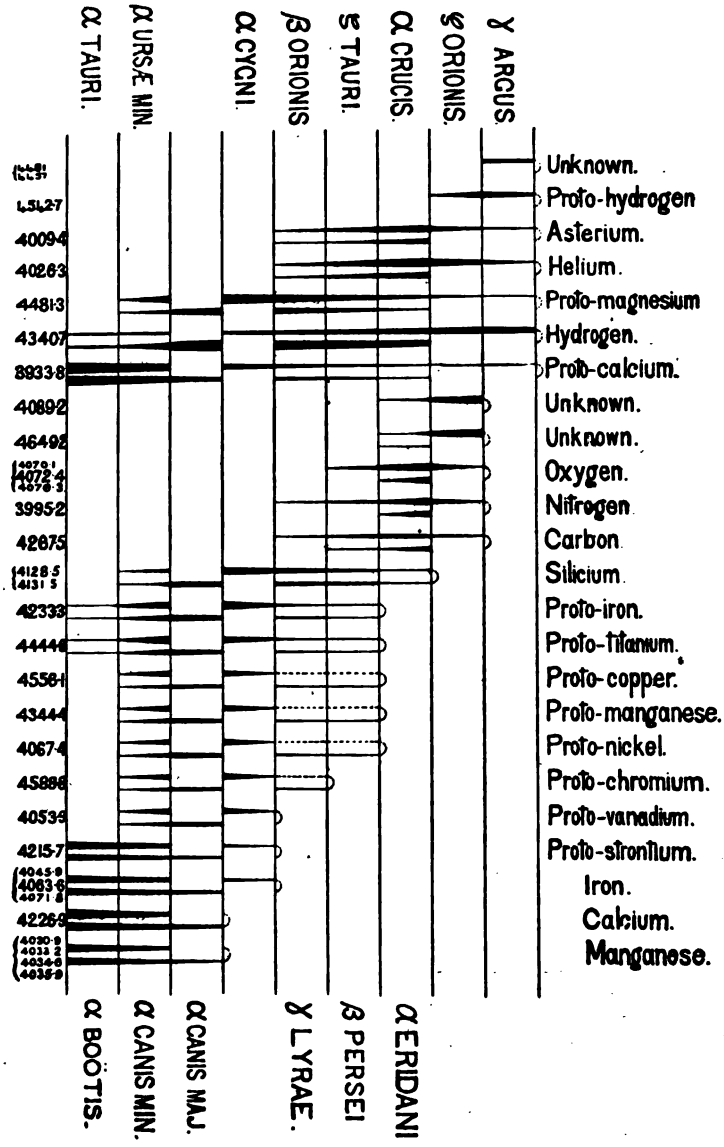
TABLE III.

Origin.	λ of chief lines.	Range in ascending series of stars.	Range in descending series of stars.
Unknown	4457 4451 3876	Seen only in γ Argus.	
Hydrogen (new) ..	4544·0 4200·4	ζ Orionis to γ Argus	No stars available.
Unknown	4089·2	α Crucis to ζ Orionis	
„	4649·2	„ „	α Eridani.
Helium	4471·6 4026·3	Rigel to γ Argus	α Eridani to γ Lyræ.
Asterium	4388 4009	„ „	α Eridani to γ Lyræ.
Hydrogen	Complete series	Aldebaran to γ Argus	α Eridani to Arcturus.



curve are derived from the observed appearance and intensity of the lines, noted in the different stars.

The wave-lengths of the lines discussed are shown at the bottom of the map.

Addendum.

The facts embodied in the map present to us the spectral changes noted in stars of Groups III., IV., and V., of my classification (*Roy. Soc. Proc.*, 1887, vol. xliii.,

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p. 117), and are a result of a more general inquiry than those referred to in my previous papers (*Roy. Soc. Proc.*, 1888, vol. xliv., p. 1; *Roy. Soc. Proc.*, 1889, vol. xlv., p. 380; *Phil. Trans.*, A., 1893, vol. clxxxiv., p. 725), the origins of a very considerable number of stellar lines having since then been traced to enhanced lines of metals and to known gases.

It will be seen that this more general inquiry entirely justifies the prior statement (*Roy. Soc. Proc.*, vol. lxi., p. 182), that the metallic lines are thickest in stars increasing their temperatures, and that the hydrogen lines are thickest in stars decreasing their temperatures; in other words, on the opposite arms of the temperature curve. I have already stated a possible explanation (*Roy. Soc. Proc.*, vol. lxi., p. 183).

It will be observed that, so far, I have not been able to find stellar spectra on the downward side corresponding to those of γ Argus and ζ Orionis; but it is more than probable that near the apex of the curve only a small change will be observed; their default, therefore, is of less consequence than it might have been.

The same remark applies to α Cygni and Sirius; but here it is certain that the differences in the relative intensities of the gaseous and enhanced lines will be considerable, judging from what happens above and below the heat stages represented by them.

The stars used in the discussion give us very definite results, showing that the various chemical forms are introduced at six very distinct heat levels.

I next proceed to make some remarks upon the series of facts now for the first time brought together; it must, however, be borne in mind that all the chemical elements and all parts of the spectrum have not yet been included in the survey.

1. Hydrogen appears throughout both series of stars from top to bottom. Proto-magnesium and proto-calcium follow suit very nearly; but the highest intensity of the former is reached at the stage represented by α Cygni, and of the latter at the solar temperature represented by α Tauri and Arcturus.
2. With the above exceptions, all the chemical forms so far traced are relatively short-lived.

This is the first important differentiation. In the light of (1) we are justified in assuming that the substances in (2) would be visible in the stellar reversing layers if they were there.

3. In the stars of higher temperatures we deal generally with gases. Below the stages represented by β Orionis and γ Lyræ we deal with proto-metals and metals, hydrogen being the only exception.
4. The proto-metals make their appearance at about the same heat-level at which the gases (with carbon), always excepting hydrogen, begin to die out.

This is the second important differentiation. It is interesting to notice the distinct difference of behaviour of carbon and silicium in the descending series; the former goes through the same stages as oxygen and nitrogen, the latter behaves like the proto-metals.

5. With the exception of iron the metals, as contra-distinguished from the proto-metals, only make their appearance in stars at and below the heat-level of Sirius.

This is the third important differentiation. It is accompanied with a notable *diminution* of hydrogen and proto-magnesium, and with an *increase* of proto-calcium: indeed the latter seems generally to vary inversely with the hydrogen.

In all these changes we seem to be brought into presence of successive polymerisation due to reduction of temperature. Of the origin of proto-magnesium and proto-calcium the stars as yet tell us nothing, but it is difficult to believe that the earliest forms of the other metals are not built up of some of the constituents of the heat ranges represented by those between γ Argus and α Crucis.

The question arises whether the order of visibility at reduced temperatures now indicated does not explain the absence of proto-hydrogen, oxygen, and nitrogen from the spectra of the sun and nebulæ, the metals present in, and the absence of quartz from, meteorites, and the similarity of the gaseous products obtained from them and metals, native and other, in vacuo at high temperatures.

I have finally to express my obligations to those who have aided me in the present inquiry. For some of the metals used I am indebted to Mr. George Matthey, F.R.S., who has kindly placed the resources of his establishment so entirely at my disposal that I feel it is impossible to thank him sufficiently. For the determination of wave-lengths and the correspondence of terrestrial and stellar lines, Mr. Baxandall is responsible, while Mr. Fowler has assisted in the determination of the various stellar groups. The photographs of the enhanced lines obtained by the use of the Spottiswoode coil have been taken by Mr. Butler. The actual construction of the map from the available photographs has devolved upon Mr. Baxandall, Dr. Lockyer co-operating in the case of stars of the highest temperature.

NOTES ON THE ELECTRO-DEPOSITION OF VANADIUM.*

By SHERARD COWPER-COLES, M.Inst.M.M.

VANADIUM has not received the attention it deserves at the hands of electro-metallurgists. Vanadium oxidises slowly in the air, and has a very high melting point, about 2000° C. (equal to 3600° F.), and is neither volatile nor fusible when heated to redness in hydrogen. Vanadium is widely distributed (see "Mineral Industry," vol. vi.), but it is not often found in large quantities. It was first discovered by Seftström in 1830, in the iron obtained from the Taberg ores.

The metal is not readily attacked by hydrochloric acid, either when hot or cold, neither strong nor dilute sulphuric acid act upon the metal in the cold, but when heated with strong acid the metal slowly dissolves, giving a greyish-yellow solution. Both hot and cold solutions of caustic soda are without action on the metal, but when fused with the hydroxide, hydrogen is evolved, and vanadate formed. Nitric acid of all strength oxidises the metal with violence, evolving nitrous fumes and forming a blue liquid. The specific gravity of vanadium at 50° F. is 5·5, being somewhat lighter than zinc, and about twice as heavy as aluminium.

Metallic vanadium made by reduction from the dichloride in hydrogen, is a light whitish-grey coloured powder, which under the microscope reflects light most powerfully, and appears as a brilliant crystalline mass, possessing a silver-white lustre (Roscoe and Schorlemmer's "Treatise on Chemistry."

Vanadium was originally found in Mexico. Recently it has been discovered in considerable quantities near Santa Márta in Spain. In the Spanish mines, it is found associated with lead, tellurium, gold, and silver. Some of the ore contains as much as 124 lbs. of metallic vanadium to the ton.

Vanadium has also been mined on the elevated plains of the Great Chain of the Andes, where anthracite mines exist, containing two parallel inclined beds of vanadium-containing coal, from 2 to 3 metres thick and 1004 metres long. It is also found in Peru, in certain anthracite coals, which, according to analysis, contain about 4·5 per cent.

An interesting paper has recently been read before the Geological Society of Washington by Mr. W. F. Hille-

* A Paper read before the Institution of Mining and Metallurgy, March 15th, 1899.

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brand, on the distribution and quantitative occurrence of vanadium in the rocks of the United States.

Gore has endeavoured to deposit vanadium from aqueous solutions, but with unsatisfactory results. The electrolyte employed by him was one composed of vanadic acid, dissolved in pure dilute hydrochloric acid by means of an electric current, using a retort-carbon anode and a platinum cathode; the gas set free at the anode was observed to have a smell of ozone. He also tried a solution of dilute sulphuric acid with pure vanadate of ammonia, and electrolysed the solution with platinum electrodes. The electrolyte turned a bluish-black colour at the cathode, and a jet-black powder of some thickness was deposited upon it.

Schicht dissolved vanadium chloride in water containing hydrochloric acid, and electrolysed the solution. Inert deposition took place in the blue liquid, the vanadium acid being merely reduced to oxide.

The author has succeeded in obtaining brilliant metallic deposits of vanadium, the colour being almost as white as that of silver, from a solution prepared as follows:—

The vanadic anhydride, V_2O_5, was boiled with an excess of caustic soda, the sodium vanadate thus formed being decomposed by an excess of hydrochloric acid. The proportions were as follows:—1·75 parts of vanadic anhydride (equal to 1 oz. per gallon of solution) were dissolved in 2 parts of caustic soda and 160 parts of water, to which 32 parts of hydrochloric acid was afterwards added.

The best results were obtained with a current density of 18 to 20 ampères per sq. ft., the E.M.F. at the terminals of the electrolysing cell being 1·88. The solution was worked at a temperature of about 180° F. If higher or lower current densities were used red-brown oxide was deposited along with the metallic vanadium. A reddish-brown non-adherent powder was deposited from cold solutions at the same current density. The solution when first made up was of a light greenish-yellow colour. After boiling with a carbon anode for some time it became darker, and after passing a current it turned a rich dark green, after a good deal of metal had been taken from the solution it appeared bluish. When a solution containing 2 oz. of vanadium to the gallon was electrolysed the deposit was not so white as that obtained from a solution containing 1 oz., the deposit having a steely appearance.

Vanadium is found to increase the tensile strength of iron, copper, and aluminium when added to those metals, also the ductility. The present use of the metal is almost exclusively confined to converting aniline into fixed black dyes for indelible ink, and the colouring of glass.

The present price of vanadium oxide is about £2 per pound. Sir Henry Roscoe some years ago produced a few grms. of metallic vanadium; now that the author has shown that it can be readily electro-deposited in a metallic form, it is to be hoped that new uses will be found for this interesting metal.

ON CRUCIBLE STEEL CASTINGS.

By SERGIUS KERN, M.E., St. Petersburg.

Many difficulties arise when casting hollow steel castings having a thin body,—for instance ⅜" to ½" in thickness,—especially when the rules for delivery prescribe testing the hollow castings under pressure of steam or water.

When using ordinary carbon steel, notwithstanding the usual top-heads placed on the pattern, in places where thin parts of the casting adjoin thicker places, very often the usual local flaws are discovered; when water pressure is applied, in these places the water passes in the form of fountains, drops, or mist, according to the sizes of the local flaws or cavities in the metal. Frequently chasing the metal in these places, by hand hammers, arrests the permeability of the casting; but often this is of no use, and castings are rejected.

I make my castings by using a coke crucible furnace containing four crucibles with a charge of two-thirds of a cwt. in each pot. The carbon steel castings contain on the average:—

Carbon	0·38 per cent.
Manganese	0·42 „
Silicon	0·33 „
Phosphorus .. .. .. } Sulphur .. .. }	0·06 „

The mixture for crucible steel melting is composed of 80 per cent of punchings, coming from the punchings of soft steel ship-plates, and 20 per cent of very soft puddled iron, containing about 0·06 per cent of carbon and 0·03 per cent of manganese. Before casting, into each crucible some ⅔ of a pound of silico-spiegel is introduced, containing 10 per cent of silicon and 15 per cent of manganese. Next, into every crucible taken out from the furnace, and ready for casting, 25 grms. of aluminium are thrown.

At present I apply such a system only for small castings used in ship-building; all the hollow castings intended for keeping water or steam under pressure, in actual service, are made from nickel steel.

I found, as other metallurgists have done also, that in order to get a dense steel casting in which the local flaws or contractions are brought to a minimum, the best thing is to introduce 2 per cent of nickel into the steel castings. I proceed as follows:—The crucible charge consists of 73 per cent of punchings, 25 per cent of puddled iron, and 2 per cent of nickel, sold in the form of small cubes. When melted, ⅔ of a pound of silico-spiegel and 45 grms. of 80 per cent ferromanganese, are thrown into each crucible, by a funnel, and the metal is left to stand for twenty minutes in the furnace. When taken out for casting, after this lapse of time, the crucibles are cleaned from slag, and 25 grms. of aluminium are thrown into every pot.

Tests of such steel ordinarily give about 38 tons per square inch of breaking strain and 12 per cent of elongation in a length of 2 inches.

March 16, 1899.

NOTE ON THE ATOMIC WEIGHTS OF PRASEODYMIUM AND NEODYMIUM.

By HARRY C. JONES.

The recent article by Carl von Schele (*Zeit. Anorg. Chim.*, 1898, xvii., 310), on the atomic weight of praseodymium, records the third piece of work which was done on the same problem in the last year or two. Brauner (*Proc. Chem. Soc.*, 1898, No. 191, p. 70) published the results of his determinations of the atomic weights of praseodymium and neodymium in April last, while my own results (*Amer. Chem. Journ.*, 1898, xx., 345) were published in May.

The object of this note is to call attention to the agreement between the values found by the three experimenters, working simultaneously, but entirely independently, and to the difference between their results and those of von Welsbach (*Monatsh.*, 1885, vi., 477), which were the only determinations on record a year ago. The work of von Welsbach dates from 1885, when he separated the supposed element didymium into the two constituents praseodymium and neodymium.

Brauner and myself obtained our material from Mr. Waldron Shapleigh, of the Welsbach Light Company, Gloucester, New Jersey, U.S.A. Schele, on the other hand, prepared his material from monazite furnished by Cléve. The source of the material was thus not the same in all three cases.

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After further purifying his material, Brauner determined the atomic weight of praseodymium by analysing the oxalate and synthesising the sulphate, and obtained as a mean of thirteen values 140·95, varying between 140·84 and 141·19. He obtained the value 143·63 for neodymium.

Schele, working with praseodymium oxide which he had very carefully purified, synthesised the sulphate, and found the atomic weight of praseodymium to be 140·4, as the average of five determinations which varied from 140·30 to 140·46.

The present writer also further purified the material furnished by Shapleigh until an analysis by Rowland's large spectroscope showed that it was fairly pure. The amount of praseodymium in the neodymium, and of neodymium in the praseodymium, was then determined by means of the intensity of the absorption bands. The oxalates of praseodymium and neodymium were then converted into the oxides. The superoxide of praseodymium was reduced in a stream of hydrogen to the sesquioxide, and from the sesquioxides the sulphates were synthesised.

The atomic weight of praseodymium was found to be 140·45, with a maximum-minimum difference in ten determinations of 0·16.

The mean of ten determinations of the atomic weight of neodymium was 143·6, with the same maximum-minimum difference as above.

The agreement between the three series of results will be seen best by glancing at the following table, which will also show how widely they differ from the results of von Welsbach.

	von Welsbach.	Brauner.	von Schele.	H.C. Jones.
At. wt. Pr. ..	143·6	140·95	140·4	140·45
,, Nd. ..	140·8	143·63	—	143·6

The agreement between my own value for the atomic weight of praseodymium and that found by von Schele is very close, while Brauner's value here is a little higher. The atomic weight of neodymium, on the other hand, as found by Brauner and myself, is almost exactly the same. By comparing these three values with those of von Welsbach, it will be seen that they agree much more closely with the results of von Welsbach if the latter are interchanged. The atomic weight of praseodymium found by von Schele and myself is a little lower than von Welsbach's atomic weight of neodymium, but the atomic weight of neodymium as found by Brauner and myself is identical with von Welsbach's atomic weight of praseodymium. These three pieces of work, then, make it quite certain that the original determinations of von Welsbach are not free from error, and, indeed, they were published as only tentative, and not described in any detail.

It is a striking coincidence that a problem which remained untouched since 1885 should have been taken up at the same time by three indiviuals as widely removed as Prague, Upsala, and Baltimore.

Chemical Laboratory, Johns Hopkins University,
November, 1898.

THE

USE OF THE TRANSITION TEMPERATURES OF COMPLEX SYSTEMS AS FIXED POINTS IN THERMOMETRY.*

By THEODORE WILLIAM RICHARDS and JESSE BRIGGS CHURCHILL.

In a brief paper upon the transition temperature of sodic sulphate (*Am. Journ. Sci.*, 1898, vi., 201; also *Zeitschr. Phys. Chem.*, xxvi., 690), we have recently shown that this non-variant point is capable of being reproduced in practice with great certainty, and that it is therefore admirably suited for use as a standard of reference in thermometry. We pointed out the fact that many other systems composed of two or more components might answer equally well, and declared our intention of fixing as many points as possible in order to simplify the accurate measurement of temperature. The subsequent appearance of a hastily written note by Messrs. Meyerhoffer and Saunders (*Zeitschr. Phys. Chem.*, October, 1898, xxvii., 367), claiming for themselves a part of this scheme, has prompted the present paper, which has as its object a more detailed statement of the plan.

It is obvious that, while any number of components might be employed simultaneously for this service, the simpler systems will be on the whole the most useful. Water is so omnipresent as to be difficult to exclude from any kind of experiment; hence the investigator is almost forced to adopt it as one of the components. The choice is then of the other material or materials, and the first step was obviously to study all common substances with a view to discover the probable usefulness of the transition temperatures of their aqueous crystals. If a complete temperature scale could not be built up from such simple data it would obviously become necessary to investigate quintuple points, of which a very great number could be devised. This additional complication could not but be regretted, however; for it involves the necessity of preparing two salts instead of one in a pure state, it renders less easy the use of the same material over and over again, and it introduces a complication which might seriously retard the speed of attaining equilibrium, and hence the constancy of the desired point.

After studying with care the published records of all the field of inorganic chemistry, about two dozen salts were selected as probably suitable for the work in hand. Of these magnesic and nickelous sulphates, calcic and nickelous nitrates, nickelous chloride, and borax were rejected as being too inconstant in their indications. The lack of constancy was due sometimes to the smallness of the latent heat of transition, and sometimes to a superabundance of crystalline hydrates. On the other hand, at least eight of the new salts gave results comparable in certainty with those given by the ever trustworthy Glauber's salt. These salts are given in the the table below:—

Transition Temperatures of Nine Salts.

Salt.	By mercury thermometer.	By hydrogen thermometer.
Sodic chromate, $Na_2CrO_4.10H_2O$ ..	19·93	19·85
Sodic sulphate, $Na_2SO_4.10H_2O$ ..	32·484	32·379
Sodic carbonate, $Na_2CO_3.10H_2O$ ..	35·2	35·1
Sodic thiosulphate, $Na_2S_2O_3.5H_2O$ ..	48·1	48·0
Sodic bromide, $NaBr.2H_2O$	50·8	50·7
Manganous chloride, $MnCl_2.4H_2O$ ..	57·9	57·8
Strontic chloride, $SrCl.6H_2O$	61·1	61·0
Sodic phosphate, $Na_3PO_4.12H_2O$ ..	73·5	73·4
Baric hydroxide, $Ba(OH)_2.8H_2O$ ..	78·0	77·9

The temperatures given above are only approximations, and are subject to future revision; at this stage of the work our effort has been only to determine if the points were constant, and not to fix their absolute value. Besides these nine, several other salts promise well. Baric hydrate, given above, was our first trial of three components, for the carbonate was naturally allowed to be present. The study of such quintuple points has now been interrupted by Messrs. Meyerhoffer and Saunders's claim.

These gentlemen studied in a very hasty fashion the transition temperature of Glauber's salt in the presence of an excess of common salt. Although theoretically sound, such a system labours under a serious practical disadvantage; for the addition of heat to it means the dissolving of common salt as well as the melting of crystallised sodic sulphate and the depositing of anhydrous material. The first of these processes is obviously less speedy than the others, and must surely occupy appreciable time even if the solid is finely powdered. Such a "lag" inevitably

* Contributions from the Chemical Laboratory of Harvard College. From the *Proceedings of the American Academy of Arts and Sciences*, vol. xxxiv., No. 10, January, 1899.

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affects the temperature; our own experience with this mixture as well as with other similar ones supports this inference, and is anything but reassuring. Indeed, we found that Glauber's salt itself did not give absolutely accurate results if it were allowed to "freeze" instead of to "melt," for a similar reason.

We agree with Messrs. Meyerhoffer and Saunders as to the great desirability of uniting upon some normal temperature for the graduating of flasks, &c., but we cannot conclude with them that 18° is the best temperature. In America the steam-heated winters and sun-heated summers raise the average temperature of our laboratories at least to 20°, and indeed this temperature is more comfortable than 18° unless one is performing active manual labour. Hence at Harvard we have settled upon 20° as the normal room temperature. Sodic chromate (19·85) clearly gives us very nearly the standard of reference which we desire. In determining the specific gravities of liquids, a temperature *above* that of the room is preferable to one *below*—for the expansion of the liquid during the drying of the exterior of the pycnometer is otherwise apt to be troublesome, hence 18° is not suitable for this purpose. The authors before mentioned suggest the use of a bath of mixed salts as a means of keeping the temperature constant during determinations of electrolytic conductivity; but it should be pointed out that in such work the neighbourhood of a very large amount of a good electrolyte is necessarily risky, except in the best of hands. This is especially the case when the substance effloresces to form a fine powder, easily wafted around by currents of air. In short, while for some work with closed vessels demanding the greatest accuracy such a bath may be invaluable, the Ostwald thermostat is the safest and most convenient appliance for preserving a constant temperature in the laboratory. The baths of "melting" crystals will find their greatest use in the standardising of thermometers at fixed points; and these thermometers will continue to serve as the most handy means of attaining and registering any desired temperature. It is obvious that if a thermometer is standardised under exactly the conditions imposed upon it during its use, the correction for the cool column projecting into the air may be omitted. This correction, by the way, may account for the fact that Meyerhoffer and Saunders found the transition temperature of sodic sulphate to be only 32·35°* instead of 32·38°.

We are much pleased that the idea should have been grasped with such eagerness in the laboratory of Professor van 't Hoff, for no better proof could be found of its unquestionable utility. We feel too that constants of this sort, like atomic weights, should be studied by more than one set of investigators, and that they should be finally investigated with the utmost care in the Bureau Internationale des Poids et des Mesures, and the Reichsanstalt; hence we are glad to accord to Messrs. Meyerhoffer and Saunders the right which they demand to investigate quintuple points involving sodic sulphate or sodic carbonate. At the same time, we feel that our undoubted priority (our preliminary paper having been finished early in June) allows us to study any desired portion of this field; and for the present, feeling that the simpler systems are the better ones, we shall investigate primarily the salts named above.

Synthesis of Hydroxylamine.—A. Jouve.—Hydrogen and nitric oxide in presence of platinum react in the well-known manner, $NO+5H=NH_3+H_2O$. The author has observed that under certain conditions the reaction may be $NO+3H=NH_2-OH$. The product of the reaction is received into dilute hydrochloric acid, from which the salt of hydroxylamine is obtained. Excess of hydrogen decomposes the hydroxylamine, which is therefore an intermediate product in the reduction of nitric oxide to ammonia.—*Comptes Rendus*, cxxviii., No. 7.

* By a clerical error, Rimbach's table for this correction was stated in our last paper to be on page 143 of Landolt and Börnstein's tables (1894). It is really on page 95.

AN ACOUSTICAL METHOD FOR THE DETERMINATION OF THE MELTING-POINT OF FATS AND WAXES.

By EDWIN DOWZARD, F.C.S.

Numerous methods have been proposed for the determination of the melting-point of fats and waxes. In some the melting-point is the temperature at which the fat undergoes a certain degree of softening, either sufficient to allow a plug of the sample contained in a cylindrical tube to be forced up by the pressure of water, or to allow the sample to form a globule.

When a capillary tube is used there is some uncertainty as to whether the melting-point is that temperature at which the fat commences to liquefy, or that at which it becomes clear and transparent.

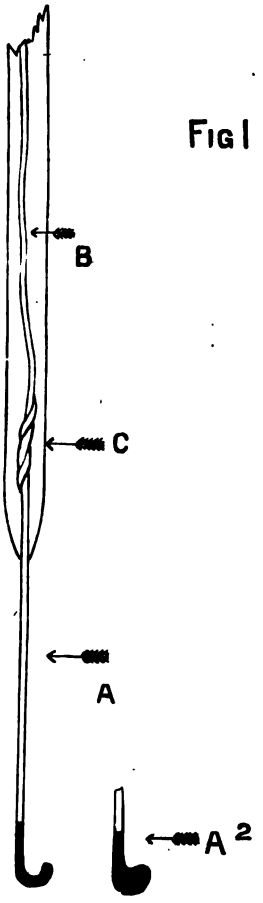

Fig I

On the Continent Pohl's method is frequently used. The bulb of a thermometer is immersed in the melted sample, and quickly removed, so that a thin coating only of fat adheres to it. After several hours the thermometer is inserted into a test-tube so that the bulb is at a distance of half an inch from the bottom; heat is then gradually applied, and the temperature noted at which a drop of liquid fat is observed to form at the bottom of the bulb.

In nearly all the methods that have been proposed there is the method of personal equation.

The method about to be described, which eliminates the error due to personal observation, is based on the following:—Two platinum wires, connected to a battery

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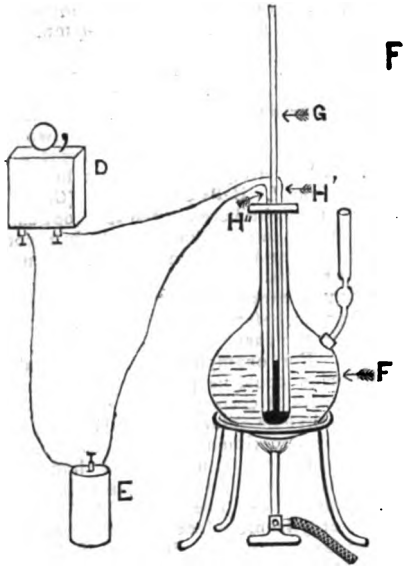

FIG 2

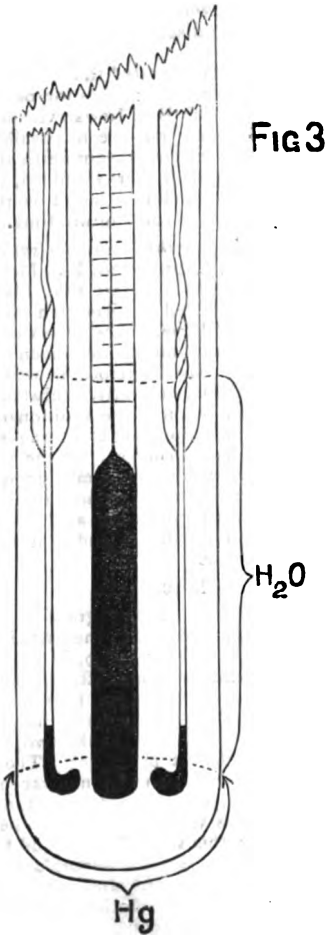

FIG 3

and electric bell, are coated with the fat or wax, and immersed in mercury, which is gradually heated; when the fat melts, the circuit is closed, which is indicated by the ringing of the bell.

Fig. 1, which represents the actual size of the original, consists of a piece of stout platinum wire (A) with a crook at the extremity, fastened to a long piece of copper wire (B); the platinum wire is fused into the glass tube (C), which is about 10 inches long. In the apparatus about to be described there are two of these wires identical in size and shape. The *modus operandi* is as follows;—The sample of fat or wax is melted in a small capsule, the platinum wires are dipped into the melted sample, taken out, allowed to cool, and the process repeated about three times; the wires will then have the appearance of A^1, Fig. 1. The coated wires are allowed to stand for three or four hours, and then placed in the inner tube of a Anschutz and Schulze melting-point apparatus, Fig. 2 (F), along with a thermometer. A quantity of mercury is now introduced into the inner tube, sufficient to allow the wires to be immersed to the top of the crook; water is then poured in until the bulb of the thermometer is completely covered. The outer flask is filled with water to the same level as the water in the inner tube. The wires are now connected with the battery and bell, and the temperature gradually raised; when within about 4 degrees of the probable melting-point the temperature should rise at the rate of about 1 degree in 70 seconds. The reading is taken immediately the bell rings.

Fig. 2 represents the complete apparatus. H' H'' are the wires, and G the thermometer.

Fig. 3 represents the bottom portion of the inner tube (full size).

Of course I do not claim this method to be original, as several chemists have proposed and described various modifications in the way of apparatus.

The above is simply the description of a modified form of apparatus which I have found to give useful and constant results.

PROCEEDINGS OF SOCIETIES.

CHEMICAL SOCIETY.

Ordinary Meeting, March 16th, 1899.

Professor DEWAR, F.R.S., President, in the Chair.

MESSRS. E. Szarvasy, E. B. Fairweather, and Arnold Stevenson were formally admitted Fellows of the Society.

Certificates were read for the first time in favour of Messrs. Frank Belton, 103, Lower Seedley Road, Pendleton, Manchester; Robert D. Connell, 38, Chapel Road, Stamford Hill, N.; Harold Francis Carl Goltz, 7, Craster Road, Upper Tulse Hill, S.W.; Robert William Lindsey, 22, Hilldrop Crescent, Camden Road, N.; James MacLeod, Westhill, Cardcross Road, Dumbarton; Allan Frederick Walden, New College, Oxford.

The PRESIDENT announced that he desired to present to the Society a daguerreotype of Dalton, which was one of two taken in 1842. The daguerreotype came into the possession of Mr. Dancer, a philosophical instrument maker of Manchester, who, it might be interesting to state, constructed Joule's thermometers and apparatus, and it was from Mr. Dancer's relatives that he had acquired the portrait. He felt that so interesting a memorial of such a man ought not to remain in the possession of a private individual, and it seemed fitting that its custody should be entrusted to the Chemical Society; he therefore presented it to the Society on the understanding that steps should be taken to ensure its safe preservation.

Through the kindness of Mr. S. W. Woolley, he had received an interesting card which appeared to have been used by Dalton during the meeting of the British Association at Manchester in 1842. This card bears his auto-

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graph and an embossed head. Accompanying it was an engraved sheet of symbols representing atomic combinations, which had been prepared to illustrate a paper read by Dalton at this meeting. These he also desired to present to the Society, to be included in the collection of memorials of illustrious chemists which was being gradually formed.

On behalf of the meeting, Professor TILDEN thanked the President for the gift of the daguerreotype, which would be preserved with all the care and solicitude which such an interesting memorial deserved. He added that he believed the well-known portrait of Dalton engraved by Jeans, and appearing as the frontispiece in Roscoe and Schorlemmer's "Treatise on Chemistry," was prepared from a drawing made from this daguerreotype.

Of the following papers those marked * were read:—

*42. "*The Boiling-point of Liquid Hydrogen as determined by a Rhodium-platinum Resistance Thermometer.*" By JAMES DEWAR, LL.D, F.R.S. (See p. 133).

*43. "*Influence of Substitution on Specific Rotation in the Bornylamine Series.*" By M. O. FORSTER, Ph.D., B.Sc.

Certain alkyl derivatives of bornylamine have been prepared, in order to ascertain the effect produced by substitution on the specific rotatory power of the base. The following observations have been made:—

1. The specific rotation of bornylamine is largely increased by the replacement of a single hydrogen atom in the amino-group by an alkyl radicle.

2. In ascending the homologous series of monalkyl derivatives, a maximum specific rotation occurs at the ethylic term; if the molecular rotation is considered, the maximum appears at the propylic term.

3. A maximum specific and molecular rotation, occurring at the ethylic term, is also met with in the two series comprising the hydriodides and the benzoyl derivatives of the homologous bases.

4. The specific rotation of bornylamine is slightly increased on replacing both hydrogen atoms in the amino-group by alkyl radicles, but the magnitude of this increase is inconsiderable when compared with that produced by substituting an alkyl radicle for a single atom of hydrogen.

5. The specific rotatory power of paranitrobenzylbornylamine approximates more closely to that of benzylbornylamine than does that of the orthonitro-compound, but this does not apply to the molecular rotation.

6. When an alkyl group replaces hydrogen of the ammonium radicle in the series of alkylbornylammonium iodides, the specific rotatory power of bornylamine hydriodide, instead of undergoing increase in the positive direction, becomes reduced to feeble lævorotation.

7. The monalkylbornylamines, although strongly dextrorotatory, give rise to benzoyl derivatives which are strongly lævorotatory.

The following bases have been prepared and examined. *Methylbornylamine*, *dimethylbornylamine*, *ethylbornylamine*, *diethylbornylamine*, *normalpropylbornylamine*, *isopropylbornylamine*, *butylbornylamine*, *benzylbornylamine*, *orthonitrobenzylbornylamine*, and *paranitrobenzylbornylamine*. Certain salts of these compounds have been also characterised.

DISCUSSION.

Dr. ARMSTRONG said that mere simple relations of mass were by no means the sole controlling influences in the case of other properties, and it would be surprising had optical activity been found to be an exception to the rule. In all experiments on optically active compounds it was difficult to discount the effect of association which, as other workers in the field had suggested, might afford an explanation of divergencies in a series of homologues such as those recorded by the author. The marked differences in the rotatory powers of the alkyl- as compared with the dialkyl-bornylamines, was only an additional illustration of the fact that asymmetry has an influence entirely different from that of symmetry on the properties of substances.

Dr. LEWKOWITSCH suggested that interesting results would be obtained if the author were able to prepare a homologue of dimethylbornylamine methiodide in which the two methyl groups were replaced by two different alkyl groups of greater mass, say, by propyl and butyl respectively. The nitrogen would thus become asymmetric, and as, from Le Bel's experiments (*Compt. Rend.*, 1890, cx., 144), it might be expected that optical activity would ensue, the examination of a product containing asymmetric carbon and nitrogen atoms could not fail to give important results.

Dr. CROSSLEY remarked that the curious behaviour of the isopropyl group, referred to by the author, was not at all uncommon in the case of ethereal salts of substituted malonic acids. For example, α-ethyl- and αα'-methyl-ethyl-pimelic acids could be prepared by the interaction of the ethereal salts of corresponding substituted malonic acids with trimethylene chlorobromide (*Trans.*, 1894, lxv., 987), but similar experiments made with the object of preparing methylisopropylpimelic acid had not given satisfactory results, and up to the present had not been completed. Another example was to be found in the preparation of ethylisopropylacetic acid from the corresponding malonate, the introduction of the isopropyl group being attended with great difficulty. It would be of interest to know what was the effect on the rotatory power of substituting dissimilar alkyl radicles in bornylamine.

Dr. FORSTER, in reply, stated that practical difficulties had hitherto prevented the examination of the derivatives of bornylamine to which Drs. Lewkowitsch and Crossley had referred. It had not been possible to prepare by direct methods either unsymmetrical alkylbornylammonium iodides or dialkylbornylamines, but this object had been kept in view, and an attempt would be made to deal with the question at some future time.

*44. "*Contribution to the Characterisation of Racemic Compounds.*" By A. LADENBURG, For. Mem. C.S.

The author refers to the fact that his definition of racemism has not received confirmation from the experiments of Kipping and Pope, but believes that the principle involved in it is correct, and has only been expressed in a misleading manner. He therefore substitutes the following:—To characterise an inactive substance, determine its solubility with and without the addition of one or other of its optically active components at the same temperature and with the same solvent. If the solubilities are different, the substance is a racemic compound; if the same, it is an enantiomorphous mixture. Experiments with racemic acid, *i*-pyrotartaric acid, and an inactive mixture of sodium ammonium *d*- and *l*-tartrates, are given in support of this view.

DISCUSSION.

Mr. W. J. POPE said he was gratified to learn that Professor Ladenburg agreed with the criticism passed by Kipping and himself (*Trans.*, 1899, lxxv., 36). upon the older work respecting the characterisation of racemic compounds. The amended form into which Professor Ladenburg cast his statement was not, however, identical in principle with the older one, as the two statements involved absolutely different principles. The older statement said that the solution of a non-racemic optically active mixture of antipodes should deposit, on crystallisation, a mixture of the antipodes of the same composition as that in solution: this view Kipping and he had shown to be untenable. Professor Ladenburg's new statement was quite independent of any similarity of composition between the mixture in the solution and that in contact with the solution; it merely embodied the principle which Kipping and he had stated, and shown to be true by experiments on mixtures of sodium ammonium dextro- and lævo-tartrates, namely, that the most soluble non-racemic

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mixture of two enantiomorphously related substances is a mixture in equal proportions. The facts (*a*) that a racemic compound had a different solubility alone than when mixed with one of its enantiomorphous constituents, and (*b*) that an inactive non-racemic mixture of two antipodes had the same solubility as a mixture containing excess of one constituent, were simple consequences of the phase rule. In case (*a*), the solution in equilibrium with the racemic compound was saturated with respect to a single substance only, but on adding one of the active components the solution became either saturated with respect to two substances—the racemic and the active—or saturated with regard to the racemic substance and partially saturated with respect to the active substance; in either case, as Professor Ladenburg found with the tartaric and pyrotartaric acids, the solution changed in concentration. In case (*b*), the solution in equilibrium with, and in contact with, the non racemic inactive mixture was saturated with respect to both *d*- and *l*-constituents, and addition of excess of one solid constituent did not affect the mixture going into solution, because it did not alter the solid phases in contact with the solution. Thus Professor Ladenburg found the solubility of a compensated mixture of sodium ammonium *d*- and *l*-tartrate to be the same as that of non-compensated mixtures; from the work of Kipping and himself it was to be premised, not only that the solutions were in both cases equally concentrated, but were both inactive, containing equal quantities of the *d*- and *l*-isomerides. He could not agree with the view that Professor Ladenburg's experiments proved that "ammonium sodium *d*- and *l*-tartrate remain uncombined in the solution"; the experiments proved merely that the *d*- and *l*-salt in contact with the solution were uncombined, but threw no light on the condition of the dissolved material. Professor Ladenburg's new statement was indisputable; it was corroborated by the work of Kipping and himself, and had nothing in common with his older definition of racemism.

Dr. Lewkowitsch suggested that the examination of a racemic compound which was more soluble in water than its optical isomerides would complement in some way the results obtained with racemic acid, which was less soluble than either dextro- or lævo-tartaric acid.

45. "*Rotatory Powers of Optically Active Methoxy- and Ethoxy-propionic Acids prepared from Active Lactic Acid.*" By Thomas Purdie, F.R.S., and James C. Irvine, B.Sc.

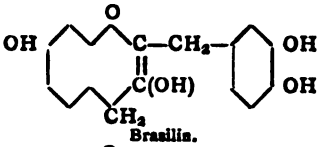
The authors have applied the method of alkylating the ethereal salts of hydroxy-acids by means of alkyl iodides and silver oxide (*Trans.*, 1899, lxxv., 157) to lævo-rotatory methylic and ethylic lactates, and have obtained methylic methoxypropionate and ethylic ethoxypropionate, the specific rotations of which at 20° were found to be $-95{\cdot}53°$ and $-79{\cdot}69°$ respectively. These high values, and the fact that the rotations are of the same sign as that of the lactates, confirm the conclusion that the alkyl lactates made from the silver salt owe their high activity to the presence of small quantities of alkyloxypropionates.

Anhydrous methoxy- and ethoxy-propionic acids, as well as ethylic methoxy- and methylic ethoxy-propionates, were prepared; the molecular rotations of the anhydrous acids were about equal to one another, and those of the methoxypropionates higher than those of the corresponding ethoxy-compounds, a result which seemed to be at variance with previous observations (*Trans.*, 1898, lxxiii., 862) on the metallic salts of the same acids otherwise obtained, according to which the methoxypropionates were the less active. The molecular rotations of the metallic salts of the two acids obtained as above, however, confirm the previous observations. Curves representing the decrease of rotation with increasing concentration show that the factor causing the decrease has a greater effect on the methoxy- than on the ethoxy-salts, and that the difference is more marked in the case of the salts of divalent metals.

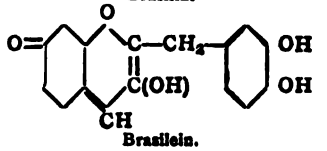
The rotations of the acids in aqueous solutions are less than in the anhydrous state, and are nearly constant on dilution, that of the methoxy-acid, as in the case of the ethereal salts, being the higher. It seems probable that the anhydrous acids contain molecular aggregates of higher activity than the individual molecules or ions, and that the higher activity of the methoxy-acid in aqueous solution, as compared with the ethoxy-acid, is due to the acid, like the salts, being more influenced by this factor.

46. "*On Brasilin and Hæmatoxylin.*" II. By A. W. Gilbody and W. H. Perkin, jun.

In continuing their investigations on the constitution of these substances, the authors oxidised dimethylbrasilin with permanganate, and obtained in this way an acid melting at 173°, which, on analysis, gave numbers agreeing with those required for the formula $C_{10}H_{10}O_6$. This acid is dibasic, the silver salt having the formula $C_{10}H_8Ag_2O_6$; it is characterised by great stability, permanganate only attacking it with difficulty at 100°; it gives no coloration with ferric chloride, but when fused with potash, and the acidified product extracted with ether, a substance is obtained which gives with ferric chloride an intense violet coloration, and is, therefore, probably resorcinol, or one of its derivatives. After a careful study of the various new oxidation products described in their previous communication (*Proc.*, 1899, p. 27), the authors conclude that brasilin and brasilein are probably represented by the formulæ—



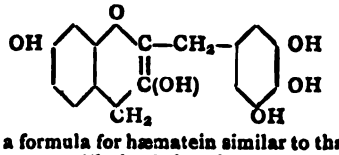
Brasilin.



Brasilein.

but they must reserve for the detailed paper the reasons which have led them to this conclusion.

If the formula for brasilin should prove to be correct, the constitution of hæmatoxylin will probably be represented by the formula—



from which a formula for hæmatein similar to that assigned to brasilein can readily be deduced.

47. "*Crystallisation of Dynamic Isomerides.*" A Correction. By T. M. Lowry, B.Sc.

In his paper on "Nitrocamphor as an Example of Dynamic Isomerism," the author states (*Trans.*, 1899, lxxv., 231) that the laws governing the crystallisation of isodynamic substances had not yet been discussed, and the behaviour of nitrocamphor and π-bromonitrocamphor on crystallisation is used as a basis for the theoretical treatment of the subject. A paper by Roozeboom, entitled "Ueber die Erstarrung flüssiger Mischungen tautomerer Stoffe," which has just appeared (*Zeit. Phys. Chem.*, 1899, xxviii., 289) has drawn the author's attention to the fact that he had unfortunately overlooked the full theoretical discussion of the subject by Bancroft in two papers on "The Equilibria of Stereoisomers" (*Journ. Physical Chem.*, 1898, ii., 143, 245). The behaviour of nitrocamphor and π-bromonitrocamphor, and the conclusions arrived at from the study of these two special cases, are completely in accord with the general laws deduced by Bancroft.

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PHYSICAL SOCIETY.

Ordinary Meeting, March 24th, 1899.

Prof. OLIVER LODGE, F.R.S., President, in the Chair.

Mr. W. R. COOPER read a paper by Mr. A. P. TROTTER on "*The Minor Variations of the Clark Cell.*"

The author describes a series of experiments in which he compared the E.M.F.'s of certain standard cells at frequent intervals from July, 1896, to February, 1897, at Cape Town, where the temperature of the double box containing the cells varied between the limits 13° C. and 28° C. One cell was selected for comparison with all the others. No special precautions seem to have been taken to keep the temperature of this selected cell constant. The observed differences between the E.M.F.'s of the respective cells rarely exceeded 0·001, corresponding to about a quarter of an inch on the slide-wire of the potentiometer. Details as to the area of the slider-contact are not stated; the readings are generally taken to the fourth decimal, *i.e.*, to one-tenth of a millivolt, and occasionally to one-fourth of this. Temperature was read to 0·1° C. on a mercury thermometer placed through a hole in the double box containing the cells—not in the cells themselves.

Mr. E. H. GRIFFITHS said that the paper appeared to have value only in so far as it showed that Clark cells at Cape Town behaved in a manner that agreed with common knowledge and general experience everywhere else. Their variations depended upon shifts of temperature, and the consequent changes in the degree of saturation of the liquid. From his own experiments during seven years, upon 42 Clark cells, he had shown that if temperature was kept constant to within 0·01° C., the steadiness and uniformity of all the E.M.F.'s was most remarkable. They started with discrepancies, but at the end of the time it was impossible to detect any differences. It was of little use to put a thermometer anywhere but within the cells; very slight changes of temperature caused serious changes in the degree of saturation of the liquid. The existence of the capricious lag of E.M.F. behind temperature precluded the possibility of formulating a temperature correction for Clark cells. In the case of Callendar cells there was no lag; their E.M.F. varied slightly with temperature, by a definite amount, which could be corrected by a coefficient.

Mr. W. R. COOPER said the method of comparison used by the author was unsuitable because to arrive at the differences of E.M.F., necessitated the measurement of the E.M.F. of each cell. The variations only amounted to a few ten-thousandths of a volt. The length of potentiometer-wire corresponding to a thousandth of a volt was only a quarter of an inch; under such conditions it would be difficult to ensure accuracy. A method of opposition would have been preferable. Mr. Cooper had found that Board of Trade cells only vary about one ten-thousandth of a volt between themselves from day to day. Cells of the H form vary about one-fifth of that amount.

Prof. J. D. EVERETT then read a paper by Dr. E. H. BARTON and Mr. W. B. MORTON on "*The Criterion for the Oscillatory Discharge of a Condenser.*"

The object of the paper is to inquire how the condition for the oscillatory discharge of a condenser is modified when the ordinary differential equation of the second degree is supplemented by the terms added by Maxwell to take account of the distribution of current in the (straight) wire. The coefficients of these terms are relatively small, so that the algebraic equation giving the periods is a quadratic with small terms of higher order added. The effect of these higher terms is, first, to introduce very rapid vibrations of small amplitude; and next, to displace the roots of the unaltered quadratic. The nature of the discharge—oscillatory or non-oscillatory—may be taken to be determined by these principal roots, and the critical case is when they are equal. The condition for equality is obtained, by the property of the derived function, as a series of powers of the small coefficients of the equation, which may be carried by successive approximation as far as is desired. The paper also treats the question by an alternative and more physical method, which consists in replacing the resistance, inductance, and capacity that occur in the ordinary formula, by modified values. This gives the criterion correct to the third order in the small terms. It is shown that a condenser satisfying the critical condition on the simple formula would, when the added terms are taken into account, give an oscillatory discharge.

Prof. LODGE said that the result naturally to be expected of "throttling," viz., the increase of resistance, and decrease of self induction, due to the current keeping to the outside of the conductor, would tend rather to damp out the oscillations than to favour them.

Prof. EVERETT observed that the equation was no longer a quadratic, and that the quadratic criterion as to whether the discharge was oscillatory or non-oscillatory did not hold. The paper appeared to be consistent with itself, and he considered that the authors had satisfactorily proved, in their discussion of the equation of current, that the effect of "throttling" was to increase the tendency towards the oscillatory mode of discharge.

Prof. LODGE admitted that the quadratic criterion did not hold; he thought it most likely that the authors, who evidently had gone into the matter with care, were right. At the same time he wished to call attention to the singular and unexpected character of their conclusion. If it turned out that it was correct, *i.e.*, that there was no slip in sign, it was a result upon which he would desire to congratulate them.

The PRESIDENT proposed votes of thanks, and the meeting adjourned until April 21st.

CORRESPONDENCE.

ANALYSIS OF THE ASH OF CARDAMOMS.

To the Editor of the Chemical News.

SIR,—In CHEMICAL NEWS (vol. lxxix., p. 122) appears a quantitative estimation of the ash of the cardamom fruit by Mr. H. B. Yardley, and, to my surprise, no mention is made of the presence of manganese, which, I believe, is always present—although in small proportions—in the ash of genuine cardamoms.

In order to satisfy my curiosity upon the point, I have referred to several standard works upon Materia Medica, and I find most of them give manganese as one of the ash constituents. Thus, in Maisch's "Materia Medica" it is stated that "Ceylon cardamoms yield 15 per cent of ash, containing 0·8 per cent of manganese;" Flückiger and Hanbury's "Pharmacographia" mentions "the ash is remarkably rich in manganese;" whilst in the "Year-Book of Pharmacy" for 1898 occurs, "Shaer states that the presence of manganese in the ash of genuine cardamoms, and its absence in other species of *Amomum*, serves as a distinction."

It would be interesting to know whether Mr. Yardley confirmed these statements or not.—I am, &c.,

HERBERT BRIDGES, Ph.C.

74, Park Lane, Norwich,
March 18, 1899.

THE ESTIMATION OF POTASH.

To the Editor of the Chemical News.

SIR,—Referring to the article on "The Estimation of Potash" in the last number of the CHEMICAL NEWS (vol. lxxx., p. 135), I beg to make the following remarks:—

The described way of estimation has been used for

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years in the Official Versuchsstationen of Germany, and answers very well. There is one difference: instead of adding barium carbonate to the alkaline solution, the barium hydroxide is added at first to the acid solution (hydrochloric acid) and then ammonium carbonate, which changes the free barium oxide or the barium chloride into barium carbonate, whilst it does not act on the barium sulphate formed. This way is preferable, since the double decomposition between sulphates and the barium carbonate is not perfect in alkaline solution.—I am, &c.,

WILLY JERWITZ, Ph.D.

The Glen, Cork.

THE 32 EQUIVALENT AND ITS RELATION TO THE PERCENTAGE OF AVAILABLE SODA IN CAUSTIC SODA.

To the Editor of the Chemical News.

SIR,—Recently I had occasion to make a test of a sample of caustic soda for available soda. As the sample had been imported from England, an English test on the 32 equivalent was asked for.

Not having a special acid solution on hand, I concluded the simplest method would be to calculate from the 31 equivalent value. The following is my method of calculation:—

The molecule of NaHO on the 31 equivalent is 40, and contains 31 parts Na_2O, which is equal to 77·5 per cent. On the 32 equivalent, NaHO equals 41 and contains 32 parts of Na_2O, which is equal to 78·05 per cent; a difference of only 0·55 per cent between the two equivalents.

On referring to the tables in Lunge's "Treatise on Alkali Manufacture" (vol. ii., p. 109), I found the difference ought to be 1·02 per cent. It would appear Lunge calculates his results from the relative percentage of Na_2O in Na_2CO_3 on the 31 and 32 equivalents. This proceeding is obviously wrong for caustic soda. It seems an extraordinary thing that such an error should have been made and remained undetected by Prof. Lunge.

Of course, one may say that a difference of 0·4 to 0·5 per cent on the available soda in a caustic soda test would not make much difference. But when it is considered that on a high strength caustic soda everything over, say, 76·5 per cent, is reported as 77 per cent, and everything under the same 76 per cent, a difference of 0·4 per cent would be very often as bad to the manufacturer as 1 per cent.

Is it not time for caustic soda consumers to combine and insist on the complete abolition of the 32 equivalent?—I am, &c.,

H. A. HOOPER.

Chicago, Ill., U.S.A.

ERYTHROL TETRANITRATE.

To the Editor of the Chemical News.

SIR,—An accident, by which a chemist lost his life, happened at a tabloid factory at Dartford, on the 15th of December, 1897. He was engaged in mixing tetranitrate of erythrol, with finely powdered lactose in a mortar, when an explosion occurred.

Again, at the end of 1898, an accident was caused by tetranitrate of erythrol being inadvertently thrown into a fire, and one person was injured.

Tetranitrate of erythrol is possessed of explosive properties, and is highly sensitive, more so indeed to percussion than dynamite or gun-cotton. As it has lately come into some use, in the place of nitro glycerine, as a remedy for angina pectoris, I should be glad if you would draw special attention in your paper to the dangers attending the handling of this drug.—I am, &c.,

A. FORD, Colonel,
H.M. Chief Inspector of Explosives.

Home Office, Whitehall, S.W., March 24, 1899.

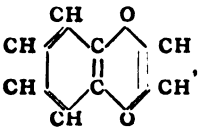
CHEMICAL NOTICES FROM FOREIGN SOURCES.

NOTE.—All degrees of temperature are Centigrade unless otherwise expressed.

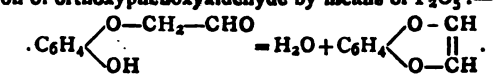
Comptes Rendus Hebdomadaires des Séances, de l'Académie des Sciences. Vol. cxxviii., No. 9, February 27, 1899.

Phosphorescence of Strontium Sulphide.—J. R. Mourelo.—The author has obtained, by the modified method of Verneuil, sulphides of strontium, calcium, barium, and zinc which present a greater and more persistent phosphorescence after exposure to diffused daylight than to the direct rays of the sun for the same period of exposure. In fact, the yellowish green luminosity characteristic of strontium sulphide is never properly obtained from specimens which have been exposed in direct sunlight. The reason is probably that the light waves of greatest amplitude exert the greatest influence, the exciting force in this case being in the invisible portion of the radiation. Radiation from the nearly colourless "Bunsen" flame and from iron heated to a temperature lower than that of redness, is sufficient to produce phosphorescence. One portion of strontium sulphide whilst phosphorescing can excite phosphorescence in another in its neighbourhood.

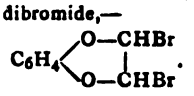
Ethylene Pyrocatechin.—Ch. Moureu.—Ethylene pyrocatechin,—



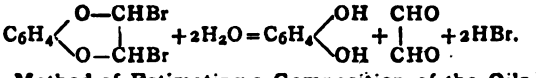
is the first body known which contains a dioxybenzene nucleus combined with an unsaturated radicle. It is obtained in very small amount by the action of acetyl chloride either on orthoxy-phenoxyacetal or on ethoxy-ethane-pyrocatechin; these methods are only of theoretical importance. In practice, it is easily obtained by dehydration of orthoxyphenoxyaldehyde by means of P_2O_5:—



Ethylene pyrocatechin is a colourless oil boiling at 193°. It readily gives the dibromide,—



when treated with HBr in a freezing mixture. This body saponifies when boiled with water, giving glyoxal and pyrocatechin, according to the following equation:—



Method of Estimating a Composition of the Oils of Acetone.—A. and P. Buisine.—The authors have devised a means of determining, as simply as possible, the composition of the oils of acetone obtained from the liquors of wool manufactories. The separation of the products, which constitute oil of acetone, is long and laborious, but it is a sufficient test of the composition to determine the density, solubility in water, solubility in acid sodium sulphite, and the volume of the liquid which distils over between known limits of temperature. The method of procedure for those determinations is indicated.

Combinations of Phenylhydrazine with Alcoholic Iodides.—P. Genvresse and P. Bonrest.—There is a violent reaction between ethyl iodide and phenylhydrazine even at low temperatures, unless the two bodies are in solution. The authors experimented with solutions of ethyl and methyl iodides respectively, and these gave with phenylhydrazine well crystallised products. Two

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products were obtained in each case; one soluble, the other insoluble in absolute alcohol. The insoluble compound had the formula $C_6H_5NH.NH.R_2I$; and the soluble compound, $(C_6H_5NH.NH_2)_2RI$.

No. 10, March 6, 1899.

Bisulphide of Tungsten.— Ed. Defacqz.— Riche's method of preparing the bisulphide of tungsten consisted in heating a mixture of equal weights of sulphur and potassium bitungstate, previously prepared by fusing the neutral tungstate and tungstic acid in the ratio of their molecular weights. The author has modified this method and devised a second. 1. *Action of Hydrogen Sulphide on Tungsten Hexachloride.*—The hexachloride is placed in a boat inside a glass tube, which is drawn out into two bulbs at one end. After completely removing the air with a current of H_2S, the tube is gently heated. The reaction begins at 375°, and the temperature is raised to 550° for some time; the bulbs are then removed and the sulphide collected. 2. *Modification of Riche's Method.*—An intimate mixture of pure dry potassium carbonate, flowers of sulphur, and the oxide WO_3 is made in the following proportions:—138 parts K_2CO_3, 464 parts WO_3, 558 parts S. The whole is put in an earthen crucible and heated in an oven, first to dull redness, then—when the reaction is over—to the fusion-point. After allowing to cool, the crucible is broken, the black mass coarsely powdered, washed with (1) cold water, (2) hot water, and finally filtered. The bisulphide obtained by the first method oxidises readily by means of aqua regia to tungstic and sulphuric acids; the other oxidises with less readiness. For analysis, the body is fused in a platinum crucible with a mixture of KNO_3 and K_2CO_3; the cooled mass is dissolved in water, acidulated with HCl, and evaporated to dryness. The residue is extracted with water; insoluble tungstic acid remains behind, and the sulphur in the solution is estimated as barium sulphate. The metal is estimated as WO_3. Prepared from H_2S and WCl_6, the bisulphide consists of amorphous black scales; prepared by the second method, it is in the form of small crystals. Heated in the air, it burns; but undergoes change of composition when heated to exceedingly high temperatures away from air. Towards 400°, chlorine readily converts it into the hexachloride.

Action of Formic Aldehyde on Menthol and Borneol.—A. Brochet.—Formaldehyde reacts with alcohols to give formals of the general formula $CH_2(OR)_2$. The author has obtained dimentholic formal, $CH_2(OC_{10}H_{19})_2$, and diborneolic formal, $CH_2(OC_{10}H_{17})_2$.

MISCELLANEOUS.

Royal Institution.—The following are the Lecture Arrangements after Easter at the Royal Institution:—Professor J. Cossar Ewart, three lectures on "Zebras and Zebra Hybrids"; Professor Silvanus P. Thompson, two lectures on "Electric Eddy-currents" (the Tyndall Lectures); Professor W. J. Sollas, three lectures on "Geology"; Professor Dewar, three lectures on the "Atmosphere"; Mr. Lewis F. Day, three lectures on "Embroidery"; Professor L. C. Miall, two lectures on "Water Weeds"; Mr. Louis Dyer, three lectures on "Machiavelli"; Mr. W. L. Brown, two lectures on "To Iceland in Search of Health"; Mr. Edgar F. Jacques, three lectures on the "Music of India and the East, and its Influence on the Music of Europe" (with musical illustrations). The Friday Evening Meetings will be resumed on April 14th, when a discourse will be delivered by Professor A. W. Rücker on "Earth Currents and Electric Traction." Succeeding discourses will probably be given by Dr. F. W. Mott, Professor C. A. Carus Wilson, Dr. W. J. Russell, Professor T. Preston, The Right Rev. the Lord Bishop of Bristol, Sir William Martin Conway, Mr. H. G. Wells, and other gentlemen.

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THE CHEMICAL NEWS.

Vol. LXXIX., No. 2054.

ON THE REDUCTION OF CHROMIC ACID BY ACETIC ACID, AND ITS EFFECT IN ANTHRACENE TESTING.

By HENRY BASSETT.

In the course of a series of experimental anthracene tests, lately carried out, some decided irregularities in the results were observed, for which it was very difficult to account. Eventually, however, they were found to arise from the acetic acid employed, and the result of the enquiry is, I believe, of sufficient importance to be put in evidence.

The acetic acid in question was of presumably good quality, and crystallised at 56° F.

I had long ago noticed that the usual chromic solution, which when freshly prepared is of a clear red colour, soon became browner and less transparent, indicating slight reduction; I therefore made comparative experiments with the acid referred to, and with the best acid crystallising at 62° F., and found very marked differences between them.

Two solutions were prepared exactly as used in the ordinary test (with chromic acid of 98 per cent), one with the acetic acid crystallising at 56°, the other with pure acid crystallising at 62°.

These solutions were analysed at intervals of a few days, and the reduction gradually increased in both cases, but much more slowly with the pure acid. After 24 days it represented a loss of 0·16 grm. chromic acid with the pure acetic acid, and to no less than 0·87 grm. chromic acid when using the inferior acetic acid, out of the 15 grms. used for a test.

These results indicated the presence of small quantities of aldehyde, acetone, &c., in the inferior acid, which was confirmed by its behaviour with silver salts.

It then became necessary to find out what reduction took place in a boiling solution. Experiments were made with the pure and inferior acetic acids precisely as in ordinary anthracene testing; *i.e.*, with exactly the same proportions of chromic acid, acetic acid, and water, but *minus* the anthracene. After four hours' boiling the reduction was found to correspond to 4·44 grms. chromic acid with the pure acetic acid, and to 6·45 grms. with the inferior acid (calculated as before on to the 15 grms. used for a test).

These unexpected results led me to try the effect of more or less water; in a few words, with equal volumes of acid and water the reduction became almost *nil*, but, on the other hand, by using pure acetic acid without any water, after boiling for about ten hours the solution on cooling became a mass of crystals of chromic acetate, and the reduction was found to have extended to more than two-thirds of the total quantity! The same formation of crystals, &c., was obtained with the usual proportion of water, but only after boiling for, say, 48 hours.

The generally accepted statements in text-books, that acetic acid is scarcely attacked by chromic acid, are completely contradicted by these results, and it is almost unnecessary for me to point out their bearing on anthracene testing. In the first place, when using an inferior acetic acid, higher results will be obtained from the greater destruction of chromic acid during the boiling. This difference, from my experiments with the acid referred to above, amounts to (say) 0·4 per cent of anthracene.

Secondly, with inferior acetic acid the oxidising mixture will lose strength by keeping for some time. This is probably the cause of many unexplained discrepancies, as for convenience this mixture has commonly been prepared in some considerable quantity, and it is obvious that tests made with the last portions of the stock (which may have been kept a long time) will be higher than subsequent tests made with a freshly prepared mixture. My actual experimental results have given a difference of, say, 0·3 per cent of anthracene when using a mixture a month old.

Comparative experiments with pure acetic acid and freshly prepared oxidising mixture, against inferior acid and old mixture, gave confirmatory results, the difference being approximately the sum of the two above mentioned.

These results show the reason why the very large quantity of 15 grms. chromic acid should have been found necessary to oxidise 1 grm. of anthracene, much more being used up by the acetic acid than by the anthracene itself. I may add here that I have proved by analysis of filtrates from the crude quinones that half the chromic acid (say 7·5 grms.) remains unreduced.

Finally, the indications are that only pure acetic acid crystallising at, say, 62° F. should be used, and that the oxidising mixture should not be more than 15 days old.

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MISCELLANEOUS NOTES.

Opening up Specular Iron Ores.

The specular variety of hæmatite, such as is mined in Elba, for instance, contains crystals of ferric oxide which, though easily crushed to small laminæ, are not easily ground, even in an agate mortar, so finely as to be quite soluble in acids. The glistening of the small plates is apparent when a moderate amount of patience has been exhausted in grinding enough of the ore for a complete analysis.

A preliminary fusion does not always overcome the difficulty, and it is objectionable in that it introduces a considerable amount of fixed alkaline salts; a point of some moment where great care is being taken to avoid the accumulation of such compounds in passing from the estimation of silica to the estimation of magnesia on the same sample. It cannot come amiss, then, to describe an alternative procedure which neither needs laborious grinding of the sample nor introduces material amounts of impurity.

The ore, which is sufficiently fine after passing through a sieve of 90 meshes to the lineal inch, is boiled with hydrochloric acid and diluted with some clippings of soft ashless paper which have been beaten to a pulp in water. With constant agitation this mixture is poured on to a pulp filter and washed. The pulp, which is now uniformly grey, owing to the thorough dissemination of the small crystals, is transferred to a crucible, dried, and then charred at the muffle's mouth. The crystalline ferric oxide is reduced by the glowing mass of carbonised paper as it would be in the blast furnace; but later, when the combustion of the paper is completed and the crucible is more strongly heated, the iron is re-oxidised. The glistening appearance is now gone, and except a little silica the solution is easily completed by boiling with strong hydrochloric acid.

Manganese in Chrome Steels.

Steels containing a few per cent of chromium are rarely perfectly soluble in nitric acid, and, not unfrequently, the solution cannot be completed either by long boiling or by subsequent addition of potassium chlorate. On this account, using Ford and Williams's method of estimating manganese in such steels, the precipitated manganese

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oxide is accompanied with more or less of a metallic residue. Besides the possibility of these particles containing manganese they afford a greater though less apparent source of error.

The ferrous ammonium sulphate solution by which the manganese di-oxide is to be volumetrically estimated always contains considerable free acid, must in fact have free acid present in order to complete the subsequent reaction with permanganate or bi-chromate. This free acid attacks the metallic particles, forming either more ferrous sulphate or in other ways reducing that which has been already oxidised.

Perhaps the adoption of an altogether different method is the shortest way out of the difficulty—if it is a frequently recurring one.

Chromium in Ferro-chromium.

A similar but still more subtle error may vitiate the estimation of chromium in ferro-chromium when certain processes are used. The general process referred to is the heating of the finely powdered alloy at a high temperature with strongly basic reagents so as to form chromates. The sintered (or maybe fused) mass is placed, crucible and all, into a beaker containing dilute sulphuric acid. Finally the chromic acid is titrated with ferrous sulphate and bichromate.

If any of the powdered alloy were incompletely oxidised its amount would represent not only so much loss, but by dissolving in the dilute acid solution it would reduce some of the already oxidised portion. The subtilty of the danger lies in the fact that amid the general effervescence which accompanies the contact of the acid and the ignited compound, a small error of this kind is not visibly indicated, and the small amounts usually operated upon render an error which is small absolutely of considerable moment when stated in percents.

An obvious precaution is to boil the solution with permanganate, the excess of which is destroyed by dilute hydrochloric acid after the manner of Stead's improved acid permanganate process.

J. T.

A NEW FILTERING MEDIUM.*

By GEO. WM. SARGENT and J. KIRK FAUST.

For the removal of manganese dioxide from the nitric acid in which solution it has been precipitated by potassium chlorate, a glass tube similar to that used for carbon determinations is recommended. The bottom of this tube is covered first with a small piece of glass-wool, then with asbestos. This we used for some time, but were frequently troubled by the precipitate runnning through, unless a very thick bed of asbestos was made. In this case the time consumed in filtering was very considerable, due to clogging of the filter by potassium chloride from the large amount of potassium chlorate necessary to oxidise the chromium which was present in considerable quantities in the steels dealt with.

After some experimenting we adopted the following as giving the most satisfactory results:—A carbon filtering-tube with a stem 5 inches long, and a body 3½ inches long and 1¼ inches in diameter, is filled ½ inch with pewter sand, a small piece of glass-wool being used to retain the sand; over this a thin layer of asbestos is formed by pouring in the asbestos shaken up with water and sucking the bed dry. A little hot dilute nitric acid is poured back and forth through the tube several times, when it is ready for use.

When a heavy precipitate is encountered, the bulb from a syringe is used to force air into the tube and drive the liquid through, care being taken to keep the bulb compressed until removed from the tube.

We have found that the quickest and best way to wash the manganese dioxide consists in allowing the nitric oxide to run entirely through the filter, then washing all the residue in the beaker into the tube with cold water, and, as soon as the filter is drained, washing out the potassium chloride with hot water. The filter and manganese dioxide are blown out into the beaker, and the dioxide reduced with ferrous sulphate, &c. The sand and asbestos are recovered and used time and again. The washings and nitric acid filtrate were examined and found free from manganese. In this filtrate the chromium was determined by adding ice and reducing the chromate with ferrous sulphate, &c.*

This sand filter was used for the removal of ammonium phosphomolybdate from the solution in which it was precipitated. It was found best to place a few pieces of glass rod upon the asbestos to hold it in position when the solution was first being poured upon the filter. With this device we have found the freeing of the precipitate and filter of molybdic acid to be more easily and more quickly accomplished than when paper filters were used. The phosphomolybdate has a tendency, as all know, to creep, and, unless the filter is fitted properly to the funnel, to

get into the filtrate. This trouble is avoided by the sand filter. To dissolve the precipitate, the ammonia solution is poured through the filter two or three times, and finally washed out with hot water. A number of determinations, using the sand and paper filters side by side, have been made on the same sample, and the results obtained agreed to a thousandth. It was found best to wash the sand filters, used to catch the ammonium phosphomolybdate, with ammonia as well as with nitric acid, since in the ammonia washings silica and alumina were found, and these would tend to clog the reductor.

Once made up they stand ready for repeated use, and besides saving time they save considerable money, especially where many determinations are made. By these filters one man was able to turn out in one day forty-two phosphorus determinations, and every precipitate was washed until the droppings from the tube gave no reaction for molybdenum when tested with ammonium sulphide.

* Read at the New York Meeting of the American Chemical Society, December 28, 1898.

* "Methods for the Analysis of Ores, Pig Iron, and Steel," compiled from the *Transactions of the Chemical Section of the Engineers' Society of Western Pennsylvania.*

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The cut shows clearly the manner of making up these filters.—*Journal of the American Chemical Society*, xxi., No. 3, March, 1899.

ANALYSIS OF THE WATER OF THE GREAT OR ILLECILLIWÀET GLACIER, B.C.

By FRANK T. SHUTT and A. T. CHARRON.

In August last we submitted to analysis two samples of water obtained from the Great or Illecilliwaet Glacier, B.C. These waters, collected on the 7th and 19th of August, respectively, were taken within a few feet of the Glacier's irregular face, about 1¼ miles from Glacier Station on the Canadian Pacific Railway. Throughout the summer months numberless streams of ice-cold water flow from the melting face of the Glacier, to form a foaming torrent that rushes down the valley to join the Illecilliwaet River. All who have been through the mountains will remember that the characteristic feature of the Glacier streams is their turbid—or better described as *milky*—appearance, the cause of which we have ascertained to be finely divided rock matter (principally quartzite) in suspension.

The samples, which arrived at our laboratories on August 15th and 24th, were immediately examined, with the following results:—

Chemical Analysis.

	No. 1. Collected Aug. 7. Analysed „ 15.	No. 2. Collected Aug. 19. Analysed „ 24.
	Parts per million.	
Free ammonia	0·018	0·018
Albumenoid ammonia	0·027	0·037
Nitrogen as nitrates and nitrites	0·0246	0·0442
Oxygen absorbed in 15 minutes	0·0396	0·0672
„ „ 4 hours	0·1056	0·1744
Chlorine	0·10	0·10
Total solids at 105° C.	30·8	12·0
Solids after ignition	30·8	8·0
Loss on ignition	None	4·0
Phosphates	None	None.

From the above data we may unhesitatingly conclude that the Glacier water is one of great organic purity. The samples are not identical, due no doubt to the fact that they were collected twelve days apart, and probably from different parts at the foot of the Glacier. Both analyses, however, show that, judged by the standards used in the diagnosis of ordinary potable waters, it is a water possessing a high degree of purity, and one perfectly wholesome and eminently suited for drinking and household purposes.

As received, both samples were quite murky, almost milky, in appearance. On allowing them to stand, perfect subsidence took place, leaving the supernatant water colourless and brilliant. A microscopic examination of the sediment showed it to consist of very fine rock matter, chiefly fragments of quartzite. We then (December 12) determined the "total solids" in the supernatant waters, and obtained the following data:—

	No. 1.	No. 2.
	Parts per million.	
Total solids at 105° C.	16·8	1 6
Solids after ignition	12·0	None.

We thus have proof that the "total solids" of the waters as received consisted almost entirely of *suspended* rock matter. The amounts of *dissolved* mineral and organic matter are extremely small.

The following interesting note on the geology of the vicinity of the Glacier will be read with interest. It is kindly furnished by Mr. R. G. McConnell, of the Geological Survey, Ottawa, a gentleman who for many years has worked on the geology of British Columbia:—

"The rocks in the vicinity of the Glacier are of Cambrian age, and consist largely of bluish quartzites and fine-grained conglomerates holding pebbles of quartz and felspar imbedded in a hard siliceous matrix. In addition to these, greenish and dark schists of volcanic origin also occur in the neighbourhood.

Chemical Laboratories, Dominion Experimental Farms, Ottawa, March 3, 1899.

NOTE ON THE SPECTRA OF HYDROGEN.

By THEODORE W. RICHARDS.

In a recent paper B. S. Hutton recounts some interesting experiments, which tend to show that Hasselberg's "white spectrum" of hydrogen really belongs to that substance, and not to impurities (Hutton, *Phil. Mag.*, September, 1898, p. 338). One point he was unable wholly to explain—the fact that Cornu (*Journ. de Phys.*, 1886, [2], vol. v., 100-103 and 341-354), and he always obtained a brilliant red four-line spectrum of hydrogen whenever a trace of oxygen was present. The experience recently gained by Professor Trowbridge and the writer upon this subject furnishes the data for an explanation of the matter, and the object of these few words is to remove the uncertainty (*Am. Journ. Sci.*, iii., 117 and 327; or *Phil. Mag.*, 1897, [5], xliii., 135 and 349).

We observed that water vapour under diminished pressure gives the pure red spectrum far more readily than hydrogen itself does, and that when aqueous vapour is mixed with elementary gases it seems usually to be the chosen vehicle for the transport of the electricity. Obviously water must have been formed in Hutton's and Cornu's tubes, and this must have been the source of the red spectrum. The fact that water vapour thus conducts electricity easily may be accounted for by its heterogeneous molecular constitution (compare Volterra, *Ztschr. Phys. Chem.*, 1898, xxvii., 375; also J. Zeleny, *Phil. Mag.*, 1898, [5], xlvi., 120-154, &c.), which is naturally more sensitive to electric stress than the homogeneous structure of the hydrogen molecule. This is only one of the many arguments which go to support the hypothesis that the red spectrum of hydrogen is due to dissociated atoms—or at any rate to the disturbance caused by the act of dissociation, while the white spectrum is due to a compound fracture of polarised particles. Obviously from water only the characteristic lines of atomic hydrogen, not those of molecular hydrogen, could be obtained; and these are obtained so easily that the molecular spectrum of water steps into the background. On the other hand, if the hydrogen is quite dry, as was evidently the case in some of Hutton's as well as in our experiments, the red spectrum requires tremendous heat for its appearance in a state of purity—a circumstance which hypothesis explains simply by ascribing great stability to the polarised molecular structure of the gas.

Randall has recently published a paper in which he recounts his difficulties in obtaining the pure hot red spectrum of hydrogen free from relics of the cool white one (W. W. Randall, *Am. Chem. Journ.*, 1897, xix., 682). Strangely enough he speaks of the presence of aqueous vapour as a possible cause of the existence of the white spectrum, when experimentation would have shown him that the absence of water alone makes this spectrum possible in a state of purity. He seems to have overlooked the fact that a large capacity (10,000 electrostatic units, or more according to circumstances) charged with a very high electromotive force—in other words, great current strength—is necessary in order to provide enough heat to yield the hot spectrum from dry hydrogen, even at its tension of least resistance. This tension varies from one-half to 1 m.m. of mercury, according to the current

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strength, a value in any case lower than the tensions employed by him (3 to 8 m.m.). It is very certain that an ordinary Ruhmkorff coil and Leyden jar, such as those used by Randall, could not yield the red spectrum under his circumstances, provided that the gas was dry, as his seems to have been.

It is odd that Randall, while commenting upon a supposed absence of data in our papers concerning the source of our hydrogen, should have himself forgotten to state his mode of generating the gas. His drying train seems to have included sulphuric acid, a dangerous absorbent of water where hydrogen is concerned, but this could not have effected the final result, for the gas whose spectrum he observed had been diffused through platinum. Our hydrogen was prepared by electrolysis from pure dilute hydrochloric acid, was freed from acid by large amounts of potash, and was dried by standing over phosphoric oxide.* It is needless to say that we took all the necessary precautions about sweeping out and filling the tubes, so well known to anyone who has had experience in observing the spectra of gases. One regrets that Randall should have fancied a disagreement between his results and ours, when in reality they are wholly concordant.

In the light of all the facts, and the obvious explanation of Cornu's apparent discrepancy, one can hardly doubt that Hutton and others are quite right in ascribing to hydrogen itself, and not to impurity, the "cool" white spectrum of many lines.—*American Chemical Journal*, vol. xxi., No. 2, February, 1899.

THE ESTIMATION OF TANNIN.

By LEO VIGNON.

I HAVE the honour of presenting a new method for the estimation of tannin based on the following principle:—

Given an aqueous solution of tannin, this substance, to the exclusion of all other bodies which usually accompany it (gallic acid, glucose, &c.), is easily and entirely absorbed by de-gummed silk. It suffices to maintain the silk-tannin mixture digesting for four or five hours at a temperature of 50° C., and to use a large excess of silk with regard to the tannin which should be in dilute solution (5 grms. of silk and about 0·1 grm. of tannin dissolved in 100 c.c. of water).

The tannin thus absorbed may be estimated by several methods:—

a. By Direct Weighing.—By determining the difference of the absolute weights of the silk before and after absorption.

b. By Difference.—By weighing the extract, at 110° C., of the solution of tannin before and after the absorption by the silk.

c. By Difference.—By titrating with permanganate of potash before and after the action of the silk, indigo-carmine being added to the tannin.

In this latter case, the difference found in the permanganate is converted into tannin (gallotannic acid) by applying Neubauer's coefficient of equivalence, confirmed by Sisley (1 c.c. of the solution of permanganate of potash at 3·164 grms. per litre,—

$$\frac{K_2Mn_2O_8}{100},$$

corresponds to 0·004155 grm. of pure tannin.

The process *a* is lengthy, complicated, and not very exact. The second, *b*, is simple and expeditious, and gives sufficiently good results for ordinary practical work. The third, *c*, is the most exact.

* Compare *Am. Journ. Sci.*, iii., 331; a paper published three months before the date of Randall's. Hutton also overlooked this paper.

I here give the experiments made justifying the method proposed:—

I have made estimations of tannin on samples of sumac and China gall by the new method and by a certain number of the old methods which gave the best results.

1. New method (absorption by de-gummed silk and titration with permanganate).
2. Aimé Girard's method (absorption by violin strings and titration with permanganate).
3. Sisley's method (precipitation of the tannin by ammoniacal acetate of zinc).
4. New method (absorption by silk and weighing the extracts).
5. Aimé Girard's method (absorption by violin strings and weighing the extracts).

Method.	Tannin found per cent of material. Sumac. 20 grms. of leaves, 1000 c.c. water.	Gall. 10 grms., 1000 c.c. water.
1	16·34	52·42
2	16·34	52·42
3	16·27	52·03
4	16·40	52·65
5	16·50	53·10

These results are very concordant within the limits of commercial analysis.

The method based on the use of de-gummed silk should be applied in the following manner:—

Silk.—The de-gummed silk is washed and rinsed in distilled water. It can be easily prepared by treating 20 grms. of raw silk in two successive baths of 500 c.c. of distilled water containing 50 grms. of white soap. Each bath should be used, boiling for thirty minutes. The silk is smoothed in the soap bath, wrung out after the first, and rinsed and thoroughly wrung again in distilled water after the second bath, to remove all the soap. For each estimation of tannin, we employ 5 grms. of silk (weighed to 0·01 grm.).

Solution of Tannin.—We weigh out 3 grms. of tannin in ether solution (containing about 86 per cent), 10 grms. of rich materials (gall nuts at 50 per cent), 20 grms. of medium material (sumac, oak-bark), and exhaust methodically with warm distilled water at about 60° C., filter, and make up to 1000 c.c. with distilled water measured at 50° C.

Permanganate of Potash.—The solution should contain 3·164 grms. $K_2Mn_2O_8$ per litre, and be checked with oxalic acid or ferrous sulphate.

Solution of Indigo.—Twenty grms. of superfine paste of indigo-carmine (20 per cent in 1 litre of water).

Estimation.—To estimate the tannin in a China gall-nut, 10 grms. of the gall-nut are exhausted with 1000 c.c. of water (A); 50 c.c. of A are diluted to 250 c.c. (B).

Titration of the Indigo by the Permanganate.—In a two-litre porcelain dish we place 1 litre of distilled water, 50 c.c. of the indigo solution, and 10 c.c. of pure sulphuric acid. We then add, by means of a burette with a glass tap, of 50 c.c. capacity, divided into tenths of a c.c., the permanganate solution (1 drop a second), stirring regularly until the complete decolouration of the indigo—say, 22 c.c. of permanganate for each 50 c.c. of indigo.

Titration of the Tannin in the presence of Indigo.—Take 1 litre of distilled water, 50 c.c. of indigo, 50 c.c. of tannin, and 10 c.c. of sulphuric acid; we find for decoloration:—

Permanganate	40·05 c.c.
From which we deduct for the indigo ..	22·00 ,,
That is, for the tannin	18·05 ,,

Absorption of the Tannin.—To 100 c.c. of the liquor B we add 5 grms. of de-gummed silk in an emery pounce-box of 250 c.c. capacity, and keep it in the oven at 50° for five hours (*not more*), while stirring from time to time. After cooling, the tannic liquor in which the silk is soaking is again titrated with permanganate.

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Titration of the Liquor after Absorption.—Take 1 litre of distilled water, 50 c.c. of the exhausted solution, 50 c.c. of indigo, and 10 c.c. of sulphuric acid; we found:—

Permanganate	26·80 c.c.
From which we deduct for the indigo ..	22·00 ,,
	4·80 ,,

The tannin absorbed by the silk corresponds to 18·05 − 4·80 = 13·25 c.c. permanganate. We thus deduce for the percentage of tannin (counted as gallotannic acid) present in the sample—

$$13{\cdot}25 \times 1000 \times 0{\cdot}004155 = 55{\cdot}05.$$

We have already stated that the operation might be simplified—though losing a little of its exactness—by determining the extract at 110° before and after absorption and calculating the tannin by difference.

The method proposed presents the following advantages:—The material for absorbing the tannin (de-gummed silk) is easily obtained in a state of purity. It is homogeneous, regular, and unchangeable; it is weighed and manipulated with great ease. Violin strings, on the contrary, require rather a long preparation. Powdered skins are irregular, and give up soluble organic matter to water, and are not at all to be depended upon. The absorption by silk is effected in five hours at 50°, while the violin strings and skin powder can only be used cold and take about thirty hours. Finally, the coloration of the silk after absorption enables us to estimate comparatively, to a certain extent, the coloration of the tannin; this indication is extremely useful in dyeing and tanning.—*Bull. Soc. Chim.*, Series 3, xix.-xx., No. 22.

A NEW METHOD FOR THE PREPARATION OF CHLOROPLATINITE OF POTASSIUM.

By M. VÈZES.

I. Of all the platinum compounds the chloroplatinite of potassium, $PtCl_4K_2$, is the one which is of the greatest interest from the point of view of its applications; it is, in fact, in the form of chloroplatinite of potassium that platinum is used by photographers for producing permanent positive proofs known as "platinotypes," the demand for which is constantly increasing. Now the methods used up to the present for the preparation of this salt are far from having the simplicity and economy of manufacture necessary to a truly commercial article.

Chloroplatinite of potassium can be obtained either directly from metallic platinum or from the chloroplatinate. In the first case the method most generally used is that proposed by Claus. The metal is transformed into chloroplatinic acid by solution in aqua regia, evaporation to dryness, and re-solution in water slightly acidulated with hydrochloric acid: this acid is reduced in warm dilute solution by a current of sulphurous acid gas, which changes it into chloroplatinous acid; finally the solution obtained, to which an equal quantity of chloride of potassium has been added, gives, on cooling, the crystallised chloroplatinite.

This method is, as can be seen, long and complicated, and, further, the reduction of the chloroplatinic acid by the sulphurous acid gas is a very delicate operation to perform properly, an excess of sulphurous acid being able to transform the chloroplatinous acid into difficultly destroyed platosulphurous compounds, so that constant attention and frequent tests are necessary so as to stop the current of gas at the right moment.

Besides Claus's method we may mention two others, which only differ in the method adopted for changing the chloroplatinic acid into chloroplatinous acid. In the method described by Magnus (*Ann. Chim. Phys.*, Series 2, vol. xl., p. 110) the solution of chloroplatinic acid is evaporated to dryness, and the residue heated to a temperature of about 350°. Water, hydrochloric acid gas, and chlorine are given off, and platinous chloride, $PtCl_2$, remains, insoluble in water, but soluble in warm hydrochloric acid, giving a solution of chloroplatinous acid. But, as Pigeon has shown (*Ann. Chim. Phys.*, Series 7, vol. ii., p. 446), this decomposition of the chloroplatinic acid by heat is not effected completely except *in vacuo*, in the presence of melted potash and at the temperature of boiling mercury; without these precautions, which are almost impracticable in commercial operations, the return of chloroplatinite is but mediocre.

Finally, Pigeon's method (*Compt. Rend.*, cxx., 681) consists of saturating chloroplatinic acid with carbonate of barium, and then heating the solution obtained on the water-bath with an exactly equivalent quantity of dithionate of barium. This then passes to the state of sulphate, which is precipitated, and the filtered liquor does not contain anything but chloroplatinous acid with an excess of hydrochloric acid. This beautiful method gives excellent results, but it has the double inconvenience, from the industrial point of view, of requiring very exact weighings, and also the use of a relatively expensive salt.

II. On the other hand, chloroplatinite of potassium can be also obtained from the chloroplatinate, $PtCl_6K_2$, by the direct reduction of this salt. The methods of preparation based on this principle are *à priori* the most advantageous, considering that it is in the form of chloroplatinate of potassium* that the platinum is finally found in most of the operations to which these compounds may have to be submitted; the platinum residues are, in fact, always largely composed of chloroplatinate, in the same way that those of silver are generally chloride.

It is evidently of great advantage to be able to convert the residues directly into chloroplatinite, without passing through the metallic state, in the same way that it would be very convenient to convert silver residues directly from chloride to nitrate without first bringing them to the metallic state.

Two methods have been proposed for the direct conversion of chloroplatinate of potassium into chloroplatinite. Böttger (*Journ. f. Prakt. Chem.*, vol. xci., p. 251), treated the solution of chloroplatinate with a current of sulphuretted hydrogen, which reduces a part of the salt to the state of chloroplatinite, but at the same time precipitates the major part of it in the state of sulphide; the return of chloroplatinite is therefore not very great. Thomsen (*Journ. f. Prakt. Chem.*, Series 2, vol. xv., p. 295), heats the solid chloroplatinate with a little water and an excess of cupreous chloride, which reduces it while passing to the state of cupric chloride. The solution thus obtained, separated by filtration from the excess of cupreous chloride and unreduced chloroplatinate, deposits on cooling crystals of chloroplatinite. But these crystals always retain a little copper, the separation of which requires several washings with alcohol; further, the return of chloroplatinite is not great. Groger (*Zeit. Angew. Chem.*, 1897, p. 152), has modified Thomsen's method, with regard to increased returns, by adding to the mixture powdered zinc; he thus obtained 76 per cent of the theoretical yield. But it is evident that this addition does not constitute an improvement from the point of view of the purity of the product obtained.

It can be seen from the foregoing what improvements are necessary in the commercial preparation of chloroplatinite of potassium; a simple method of reduction of the chloroplatinate, not requiring expensive reducing agents, and not requiring special precautions, and giving a good return of a product perfectly free from foreign metals.

III. We have recently shown how the chloroplatinate of potassium can be transformed into plato-oxalate by the

* The platinum residues sometimes also contain chloroplatinate of ammonium; but it is not difficult to transform this into a potassium salt by boiling with potash.

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action of an excess of neutral oxalate of potassium, in dilute, boiling solution,—

$$PtCl_6K_2+3CO_2K.CO_2K=Pt(CO_2.CO_2)_2K_2+2CO_2+6KCl.$$

On the other hand the plato-oxalate thus obtained can be easily transformed into chloroplatinite by the action of an excess of hydrochloric acid. These two reactions together thus constitute a process for the transformation of the chloroplatinate of potassium into chloroplatinite, a process fulfilling, at least partly, the theoretic conditions indicated at the end of the preceding paragraph.

This process, it is true, is not absolutely direct, since it requires the production during its operation of the plato-oxalate, which must be crystallised and separated from its mother liquor before being subsequently transformed into chloroplatinite. Further the slight solubility of the chloroplatinate in water, even when boiling, makes it difficult to effect the transformation of notable quantities of this salt into the plato-oxalate in a single operation.

IV. These inconveniences may be entirely avoided by applying an important modification, which has only recently been discovered, to the operation. This reaction (the transformation of the chloroplatinate into the plato-oxalate) may be considered to take place in two phases; in the first, the chloroplatinate is reduced by a molecule of the oxalate, from which all the carbon is eliminated in the form of carbonic acid :—

$$PtCl_6K_2+CO_2K.CO_2K=PtCl_4K_2+2CO_2+2KCl;$$

in the second, the chloroplatinite formed is transformed into plato-oxalate by exchange with the two other molecules of oxalate—

$$PtCl_4K_2+2CO_2K.CO_2K=Pt(CO_2.CO_2)_2K_2+4KCl.$$

From this it results that we ought to be able to effect the direct reduction of the chloroplatinate to chloroplatinite by producing the first phase of the preceding operation only; that is to say, by using only one molecule of oxalate for one molecule of the salt.

This has been verified by experiment; and from it has been evolved a method for the preparation of the chloroplatinite fulfilling perfectly all the theoretical conditions indicated above. In particular it requires three times less oxalate than the preceding process, and further it can easily be applied on a large scale, as it will no longer be necessary to use a quantity of water sufficient to dissolve all the chloroplatinate employed in the operation.

The method of working will therefore be as follows:—The chloroplatinate is suspended in a quantity of water, insufficient to dissolve it even when warm (1 litre per 100 grms. of chloroplatinate, for example; there would be no inconvenience in even reducing this quantity of water). We add one molecule of neutral oxalate of potassium for each molecule of the salt (say 37 grms. of crystallised oxalate, $CO_2K.CO_2K+H_2O$, per 100 grms. of chloroplatinate), and heat to boiling. The oxalate dissolves and reacts on the dissolved part of the chloroplatinate; it gives off carbonic acid gas, and the solution, at first a deep yellow, becomes red, The chloroplatinate thus gradually dissolves, passing to the state of chloroplatinite, and finally, after the lapse of several hours, the whole is dissolved: the deep red liquor obtained leaves on cooling perfectly pure chloroplatinite. The weight of the crystals thus obtained by the single operation naturally depends on the more or less concentrated condition of the liquor during ebullition; with a convenient concentration it may be more than 80 per cent of the theoretical weight of the chloroplatinite corresponding to the chloroplatinate employed. By the addition of alcohol to the mother liquors it is easy to precipitate almost the whole of the remainder of the salt.

To sum up, the preparation of chloroplatinite of potassium may be easily and economically effected from chloroplatinate of potassium by the direct reduction of this salt, held in suspension in boiling water, by means of an equivalent quantity of neutral oxalate of potassium. —*Bull. Soc. Chim.*, Series 3, vol. xix.-xx., No. 22.

NEW METHOD FOR THE PREPARATION OF CÆSIUM.*

By HUGO ERDMANN and A. E. MENKE.

Winkler (*Ber. d. Chem. Ges.*, xxiii., 53), tried to reduce cæsium carbonate with metallic magnesium, in both glass any porcelain tubes in a current of hydrogen. He, however, obtained no cæsium. Beketoff (*Bull. Acad. Petersburg*, iv., 247), states that it can be obtained in small quantities by the electrolytic reduction of the cyanide; he also acted on the hydrate with aluminum, but the yield was poor. In 1894 he made a small amount by acting on cæsium alum with metallic magnesium (*Proc. Russ. Phys. Chem. Ges.*, 1894). We made a great many experiments with a view to improving these processes, but finally found that a different method worked remarkably well, and if the directions are exactly followed it is absolutely free from danger. We found that by heating cæsium hydroxide with magnesium powder in a red-hot tube through which passed a current of hydrogen, we could obtain nearly the theoretical amount of cæsium. Inasmuch as we always commenced with cæsium alum, and as that is the cheapest and most available salt to begin with, we will give all the details of the method that we finally found to be the best. The cæsium alum should be first converted into cæsium sulphate. It is not advisable to convert it directly into cæsium hydroxide on account of the fact that too much water is required to dissolve the cæsium alum, and also because cæsium hydroxide absorbs carbon dioxide very rapidly. In order to convert cæsium alum into cæsium sulphate the following reaction can be used:—

$$2CsAl(SO_4)_2.12H_2O+3Ba(OH)_2.8H_2O=$$
$$=Cs_2SO_4+2Al(OH)_3+3BaSO_4+48H_2O.$$

Dissolve the cæsium alum in as small a quantity of boiling water as possible (it is more convenient in all operations connected with cæsium to use casseroles rather than dishes or beakers), and in a separate casserole dissolve the crystalline barium hydroxide; when both are in solution, mix the two and filter rapidly with a good pump; a Buchner funnel can be used in this operation to great advantage. The filtrate if slightly alkaline, due to an excess of barium hydroxide, should be treated with carbon dioxide for a few minutes and quickly re-filtered. It can now be either evaporated to dryness or crystallised. The next step is to convert the cæsium sulphate into cæsium hydroxide.

$$Cs_2SO_4+Ba(OH)_2.8H_2O=2CsOH+BaSO_4+8H_2O.$$

The sulphate is quite soluble in hot water, and as small a quantity of the solvent as possible should be used. The barium hydroxide should also be separately dissolved in a very small quantity of water. When both are in solution mix and filter with a suction-pump and Buchner funnel. The filtrate is rapidly evaporated to dryness in a silver crucible and then fused; it should now be poured into a silver dish so that it will make a thin brittle cake of cæsium hydroxide, which must not be exposed to the air longer than is absolutely necessary; it is quickly broken, transferred to a warm dry bottle, and weighed; then put into a hot porcelain mortar, broken into small pieces about half the size of a pea, and mixed with one-half of its weight of magnesium powder (the magnesium powder must be previously heated in a current of hydrogen to get rid of the fat with which it is always mixed); the mixture is then quickly dropped into a clean, dry, rust-free malleable iron tube of the following dimensions: 1 metre long, 15 m.m. diameter, 3 m.m. thick, and 15 c.m. from the end it is bent to an angle of about 125°. In order to keep the mixture in the tube a small bundle of clean piano wire irregularly twisted together is forced into

* Read by title before the New York Meeting of the American Chemical Society, December 28, 1898. From the *Journal of the American Chemical Society*, vol. xxi., No. 3.

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the tube down the long part to the angle, before dropping in the mixture. In filling the tube it is best held inclined. The tube is now laid in a slightly inclined combustion furnace, to aid the flow of the liquid metal and quickly connected to a Kipp hydrogen generator. The hydrogen must be passed through permanganate solution in order to oxidise hydrogen arsenide, and then thoroughly dried by sulphuric acid and phosphoric anhydride; the bent end of the tube is immersed in liquid paraffin to the depth of about 2 c.m. It is advisable to have the paraffin in a casserole about 7½ c.m. in diameter. To begin the distillation, light the burner farthest away from the mixture (the tube should never be more than one-third full), and allow hydrogen to pass through at the rate of about 40 bubbles per minute. When the temperature has risen as high as one burner can produce, light the next, but do not turn on full pressure immediately; this process must be continued, burner by burner, until reaction begins. This is readily marked by an increase in the speed of bubbling through the paraffin. If the bubbles come faster than 80 to 100 per minute, turn out the last lighted burner and remove the tile over the tube. Bubbling will now gradually cease, due to the probable formation of hydride of cæsium, decomposed at high temperatures; consequently the hydrogen pressure must be increased until gas comes through the paraffin. When the back suction is relieved the hydrogen stream can be restored to its normal rate. This operation must be continued until all the burners are lighted and the temperature is full red. The angle piece of the tube, which should be as close to the furnace as possible, is now heated by a powerful Bunsen burner, and constantly struck with a piece of iron. The metallic cæsium which has distilled into this part of the apparatus, will be liquefied, and will trickle down under the paraffin, collecting in silvery drops. The cæsium comes out of the tube at the very end of the process and not before. If the foregoing directions are closely followed the whole operation can be accomplished in four hours without the slightest difficulty or danger. Explosions only occur when the tube is heated too rapidly, and not sufficient attention paid to the pressure regulation. It is evident from the result of these experiments that Winkler was mistaken in stating that it is impossible to obtain cæsium from its compounds by the aid of magnesium. We made cæsium in quantity by our method and are now studying its physical properties.

A REVISION OF THE ATOMIC WEIGHT OF NICKEL.*

Second Paper.—The Determination of the Nickel in Nickelous Bromide.

By THEODORE WILLIAM RICHARDS
and
ALLERTON SEWARD CUSHMAN.

In a recently published investigation upon the atomic weight of nickel we gave three series of results, depending upon the ratios of silver and of argentic bromide to nickelous bromide (*Proc. Amer. Acad.*, xxxiii., 97). These led us to the conclusion that the atomic weight in question could not be far from 58·69 if oxygen is 16·000. Since, however, no single method is ever convincing, and since the results above mentioned did not represent all that might be done even with one method, it was evidently advisable to pursue the matter to a more definite conclusion. Accordingly, we determined to continue the work with a two-fold object in view; first, to study further the preparation of pure material, and secondly, to complete the analysis of nickel bromide in such a way as to *determine directly the amount of nickel as well as the amount of bromine in the salt.* No surer test of a quantitative result than such a complete analysis is known. The careful study of all the conditions and results has led us to the conclusion that the preparation of pure nickelous bromide is an unusually difficult problem; but the problem has been so nearly solved that we know exactly the precautions and corrections necessary to make this substance serve as an accurate basis for the determination of the atomic mass of nickel. In the light of this later knowledge we find that the results of the last paper need a slight correction, but it is satisfactory to note that the change amounts to not much over one unit in the second decimal place of the atomic weight.

While carrying out the work, we had continually in mind the various controversies which have arisen over the atomic weights of nickel and cobalt; and feeling that the "Gnomium" question raised by Krüss and Schmidt had never been conclusively laid at rest, we naturally dwelt especially upon it. Unfortunately, one cannot enter into a discussion of this subject without directly antagonising many views which have been expressed on one side or the other; but of course the following results are recorded solely in the interests of truth, without controversial bias.

The balance and weights used in the work described were the same as those described in the former paper. The weights were re-standardised, with results very similar to those found a year before. All weighings of nickelous bromide were reduced to the vacuum standard by the addition of 0·114 milligrm. per grm. to the observed weight. The specific gravity of nickel (about 8·7) is so near the specific gravity of brass (8·4) that the correction of the nickel to the vacuum standard is less than one part in a hundred thousand, hence it may be omitted.

Experiments concerning the Purity of the Materials.

The purification of our nickelous material has already been described at length (*Proc. Amer. Acad.*, xxxiii., 102). Most of the work described below was done with nickel which had been purified by Mond's process and many subsequent operations (Sample III.), but two analyses were made with a somewhat less pure sample (No. II.) made from commercial material. (See *Proc. Amer. Acad.*, xxxiii., 102 and 105). Since we had proved that further protracted treatment produced no effect on the combining weight, evidently these specimens were quite pure enough for our purpose.

Krüss and Schmidt used glassware in their preparation work, therefore it seemed worth while to make an exact observation of the well-known danger involved in this practice. To this end two very carefully treated specimens of spongy nickel were prepared, one having been made wholly in platinum, and the other wholly in the best Bohemian glass, which had been thoroughly steamed. The former of these preparations, which was supposed to be absolutely pure, left upon sublimation as bromide in a stream of bromine vapour only a very minute siliceous residue. The specimen of nickel which had been prepared in glass vessels was totally different in appearance from the one prepared in platinum; instead of being metallic and coherent, it was black and powdery. Upon the conversion of about 10 grms. of this dark powder into nickelous bromide, a beautifully iridescent voluminous residue, weighing about 5 milligrms. and consisting mainly of silica, was left in the boat. Evidently this silica had prevented the cohering or "sintering" of the metal during its original reduction from the oxide, and hence caused the pulverised state of the impure metal—a fact which is interesting as showing the great change in properties produced by a small amount of impurities.

These two experiments emphasise the well-known facts that glass is wholly unsuitable for accurate work, and that material prepared even in platinum is extremely difficult to render wholly free from silica, unless it is vapourised (compare Stas's "Untersuchungen," Aron-

* Contributions from the Chemical Laboratory of Harvard College. From the *Proceedings of the American Academy of Arts and Sciences*, vol. xxxiv., No 13, February, 1899.

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stein, pp. 269 and 279). While, however, our purest *nickel* sometimes contained traces of silica, the *bromide* prepared from it by sublimation was undoubtedly as free as possible from this impurity. Further light upon this question will be given in a following paper upon cobalt.

Although a possible contamination with silica was thus little to be feared, some other constituents of glass or porcelain were much more dangerous. All the material actually used in our analysis had been prepared wholly in platinum vessels at every stage excepting at the very end, when it had been sublimed in a porcelain tube. Obviously this tube might be attacked by the hot mixture of hydrobromic acid, bromine, and nickelous bromide vapour; but since nothing beside sodic bromide would probably sublime with the nickelous salt, and the "equivalent" of sodic bromide is almost equal to that of nickelous bromide, the slight impurity could produce no important effect upon our last year's work. This was realised at the time; and the discovery of the presence or absence of this error was one of the prearranged objects of the present paper. Since the work recorded below was completed, Professor Winkler, by a kind personal letter as well as by a recent article, wisely called attention to this flaw; and it will be seen that his objection had been both substantiated and answered before he wrote about it.

The easiest method of detecting sodic bromide in nickelous bromide is obviously to reduce the latter and then to extract the former with water from the spongy metal. Moist hydrogen easily divorces the halogen from its none too stable metallic union at a temperature of not much over 300°, at which temperature sodic bromide is essentially non-volatile. In this way repeated experiments showed that all our nickelous bromide had contained on the average not far from one-tenth of 1 per cent of sodic bromide. The particulars concerning the determination of this serious impurity naturally form an essential point in the method of analysis of the nickel salt, hence they will be found later under that head. The presence of an unreduced bromide was first detected by Mr. Baxter in the course of his work on cobaltous bromide, and some interesting details involved in its discovery will be recorded in the paper upon that subject. The amount present varied with the temperature used in the sublimation, but was otherwise surprisingly constant. The concurrent sublimation of the two salts is undoubtedly similar to the distillation of organic substances with steam, sodic bromide possessing a small constant vapour-tension at the constant temperature of about 900° used in the sublimations.

After the completion of a series of reductions of nickelous bromide containing this impurity of sodic bromide, a final attempt was made to obtain the salt of nickel in a state of absolute purity. We expected that platinum would be attacked by the mixture of bromine vapour, hydrobromic acid, and nickelous bromide, which exists in the red-hot tube during the sublimation of the salt, but platinum is the last resort in cases of this kind. In order to sacrifice as little of the precious metal as possible in our desperate experiment a large porcelain tube was lined with platinum foil,* and inside of this was placed a platinum boat containing the metal to be converted into bromide. In each of two separate specimens of nickelous bromide made in this apparatus merely a trace of sodium was found, but unfortunately enough platinum was present to render the results valueless. They are not included in the tables below. Only a small strip of the foil was injured, the very hot parts and the cool parts being alike untouched. After these experiments we abandoned the attempt to prepare absolutely pure nickelous bromide, and returned to the use of the porcelain tube for the sublimations; for sodium is an impurity much more easily weighed than platinum, under the circumstances. The only method of obviating the difficulty would have been to use a tube of nickel for the sublimation; but the obtaining and moulding of a large amount of the metal in a perfectly pure state promised to be so troublesome that we have not yet attempted this improvement.

The arrangement for supplying and purifying the large volumes of hydrogen needed in this research was gradually evolved from the simple form used in the first experiments to an elaborate piece of apparatus which will be described in detail in the paper upon cobalt.

The preparation of bromine and of the other materials has been described in sufficient detail in other papers (*Proc. Amer. Acad.*, xxxiii., 106, *et seq.*), so that no further words need be wasted upon these points. It is almost unnecessary to state that in these simple operations no loophole was left open through which an error might creep in to destroy the value of the more difficult undertaking before us. We are indebted to the Cyrus M. Warren Fund for Chemical Research in Harvard University for some of our more expensive pieces of apparatus.

The Method of Analysis.

At first many attempts were made to determine nickel by electrolysis, with the hope that nickelous bromide might be analysed in this simple and direct fashion. In order to test the method, weighed amounts of the purest spongy metal were dissolved and re-precipitated electrolytically. The spongy metal had been prepared by boiling the purest platinum-made ammonio-nitrate with much water, igniting and reducing the precipitate with pure ammonia, and heating the metal in a vacuum. The weight of nickel deposited by electrolysis always exceeded that of the pure nickel taken, hence the electrolytic method was abandoned as unsuitable for work of the highest accuracy. The excess of weight, which was noticeable even when the film was heated to 120° before weighing, and often exceeded two-tenths of 1 per cent when it was dried at 50° after the method of Winkler (*Zeit. Anorg. Chem.*, iv., 22), was traced to inclusion of mother liquor between the film and the dish, and to the probable presence of occluded hydrogen in the nickel (Raoult, *Comptes Rend.*, lxix., 826; Böttger, *Dingler's Polytech. Journ.*, 1871, cci., 80). Since the deposit was beautifully metallic and coherent in appearance, one might well have expected a better result. It is possible that these observations may help to explain Winkler's high values for the atomic weight of nickel and cobalt, since he used the electrolytic method. On the other hand, the *spongy* metal which had been used in our experiments was probably purer than that prepared in any other way, for solid impurities had been rigorously excluded, and the traces of gas present had been pumped out.

These preliminary experiments showed that the best method of determining the amount of nickel in the bromide would be to reduce it in a stream of hydrogen, provided that the reduction could be accomplished without the loss of any of the bromide by volatilisation. Following in the footsteps of Mr. Baxter's work with cobalt, it was found that moist hydrogen answered the purpose; for the temperature at which the reduction takes place is so low that no trace of nickel was found outside of the boat which originally contained the bromide, if a rapid current of the gas was maintained. It is obvious that according to the law of mass-action, the presence of a large proportion of hydrobromic acid resulting from the reduction would tend to prevent the desired reaction, and hence to facilitate the undesired sublimation; therefore a large excess of hydrogen must be present. Of course the hard glass tube used for this process was always afterwards treated internally with nitric acid, and the liquid was examined with minute care for traces of nickel.

The nickelous bromide to be analysed was contained in a platinum boat, and the method of drying and weighing it was in every respect the same as that described in detail in the previous paper upon this subject. After having been weighed, the boat was carefully placed in a hard glass tube, in which the bromide was cautiously re-

* This idea was suggested by Professor H. B. Hill. Compare also Penfield, *Zeit. Anorg. Chem.*, vii, 22.

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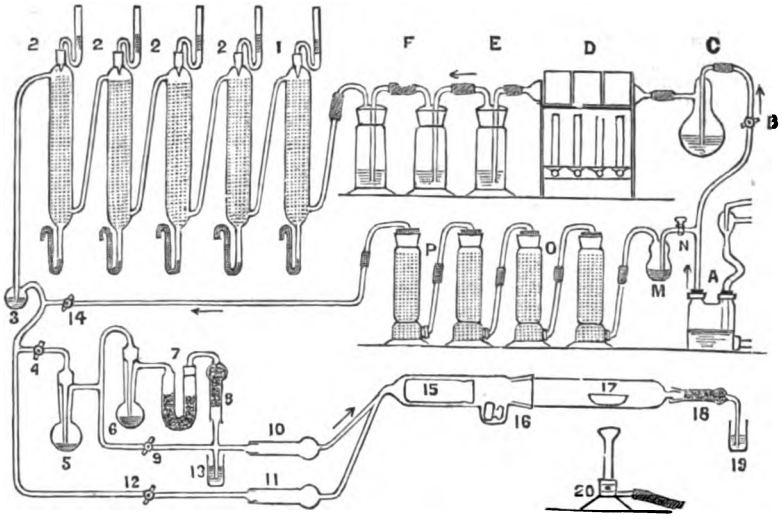

FIG. 1.—APPARATUS FOR IGNITING NICKELOUS BROMIDE IN ANY DESIRED MIXTURE OF GASES.
The use of rubber was confined to the first part of this train, where it could do no harm (A B C D E F and A M N O P).

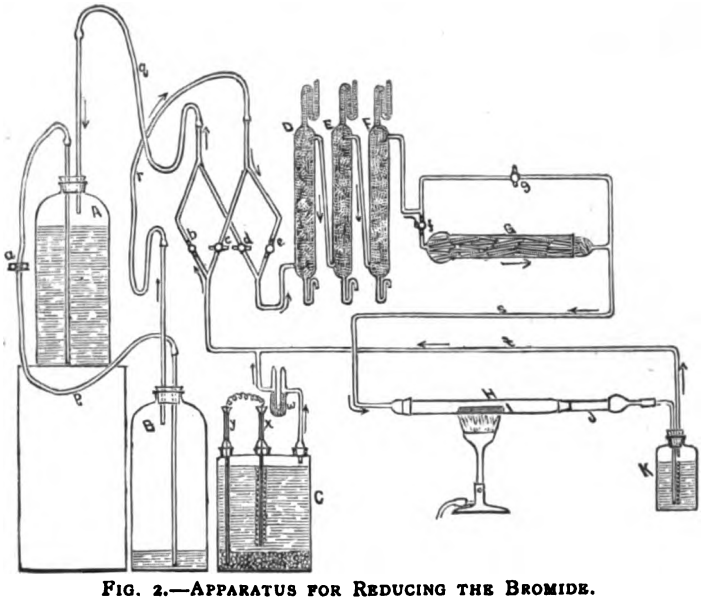

FIG. 2.—APPARATUS FOR REDUCING THE BROMIDE.

duced to the metal. When the reduction was completed and the apparatus had just cooled, the boat and its contents were returned to their weighing bottle, where they were enclosed in an atmosphere of dry air. The weight of the residue was found after half an hour, and then at the end of many hours. Since the boat was cool before having been introduced into the bottle, two successive weighings thus made never differed from one another by amounts beyond the limit of error of weighing. Spongy nickel evidently does not oxidise in dry air.

It is obviously a matter of great importance to discover whether or not the material prepared in this way contains weighable amounts of occluded hydrogen. According to the experiments of Neumann and Streintz (*Monatshefte für Chem.*, 1891, xii., 640; *Ber. der. d. ch. Gesell.*, 1872, xxv.), who worked with reduced metals, 2 c.c. of the gas were occluded by each grm. of spongy nickel. This amount would alter the observed atomic weight by only about the fortieth of 1 per cent; but since we are aiming at even greater accuracy, the matter should evidently be probed to the bottom.

In the first place, carefully weighed nickel remaining from one of the analyses recorded below was ignited in a Sprengel vacuum at perhaps 550°. For fear of losing some sodic bromide a higher temperature could not be employed. No appreciable loss of weight occurred and no gas was evolved during this process, which was repeated with several specimens; hence there seemed to be good reason to believe that no hydrogen was occluded by the metal in our experiments. In order to prove the matter, 1½ grms. of spongy nickel reduced from the bromide and allowed to cool in hydrogen was oxidised by heating in a current of dry air, which was subsequently passed over red-hot cupric oxide, and through a carefully

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weighed tube containing phosphoric oxide. Since the absorption tube did not gain in weight, no water could have been formed during the combustion, and hence no hydrogen could have been occluded.

Treated in exactly the same way, 4 grms. of nickel prepared by the reduction of the *oxide* yielded about 3 milligrms. of water or about half the amount found by Neumann and Streintz. This agreement is sufficient to show that these investigators were not mistaken in their conclusions, and that the permeability of nickel is enormously modified by minor circumstances.

Is the presence of the sodic bromide, otherwise so objectionable, the agency which prevents the occlusion in our case, or does the volatility of nickelous bromide allow its metal to be deposited in a form more coherent than that remaining from the oxide? The attempt to answer these questions experimentally would be far from uninteresting, but it is sufficient for the present purpose to prove in the manner described above that nickel treated as we have treated it in the following determinations does not occlude an important amount of hydrogen, and does not oxidise in dry air. Confirmatory evidence will be found in the paper upon cobalt which follows.

Before it was possible to use the data thus obtained for the calculation of the desired atomic mass, the weight of sodic bromide existing as impurity within the spongy metal must obviously be found. Accordingly the residue was digested with successive portions of pure water in a platinum dish, and the bromine in the filtrates was precipitated and weighed as argentic bromide. Since the spongy metal (after slow solution in very dilute nitric acid in a platinum dish) was found to contain no bromine, it is safe to infer that all the soluble impurity had been leached out by the water. This process was repeated with every analysis, the result being always the same. From the weight of argentic bromide thus obtained, the weight of the impurity of sodic bromide was calculated, and when this quantity was subtracted from both the original weight of the nickelous bromide and the weight of the spongy metal, data suitable for the calculation of the atomic mass were obtained.

In order to show that this method of correcting the results is really exact, it is necessary to prove, first, that no impurity other than a bromide remains behind in the nickel, and secondly, that no impurity beside sodic bromide is dissolved by the water. The first point has been already partially considered; we have shown that silica at least was absent (see *ante*). Since silica was the only non-volatile and insoluble acid likely to have been present, and all the bromine had been dissolved out by water, the only probable impurities were other metals capable of being reduced from their bromides by hydrogen. But these, even if they had been present in unsuspected and undiscoverable traces, could have exercised no appreciable effect upon the atomic weight unless their equivalents were widely different from that of nickel. Hence this possibility of error need cause no anxiety. Finally, it has been already stated that no weighable amount of hydrogen was ever found in the metal; hence we are justified in the assumption that the washed out spongy nickel is a safe material upon which to base the calculation of the atomic mass in question.

The question as to the purity of the sodic bromide in the wash-waters was a matter less easily settled. Careful qualitative and quantitative analysis of the liquid were alone capable of deciding the point, and with only infinitesimal amounts of material such elaborate examination was difficult. To make a very long story short, nothing was found in any of the wash-waters beside sodium, bromine, nickel, and in some of the earlier analyses traces of sulphuric acid. This last impurity may have crept in from the air during the evaporation of the aqueous solutions, or possibly from the towers used for drying the nitrogen and air. In the later analyses sulphuric acid was not used in these towers, and was proved to be absent from the nickelous bromide. As its amount was in any case very small, we felt justified in neglecting it as one neglects an infinitesimal of the second order in the course of mathematical reasoning.

On the other hand, the amounts of nickel in the wash-waters were distinctly weighable, and not to be overlooked. That it was nickel, and not a new metal, there could be no room for doubt, for it gave a black sulphide and a green sulphate, the characteristic pink colouration with potassic thiocarbonate, as well as a beautiful rose-coloured flame test, which we have found to be characteristic of nickelous halides. Since the nickel salts are much more easily reduced than those of cobalt (see the next paper), it is harder to obtain a satisfactory flame test in the former case than in the latter. Only when both salts and gas are *dry*, and the vaporisation proceeeds in the inner flame, are the best results to be obtained. We have found no reference to this flame reaction of nickel halides in chemical literature (Vogel, *Spectral Anal. irdis. Stoffe.*, pp. 246, 262), and one cannot but believe it to have been unknown to Krüss and to Winkler at the time of one of their disputes.*

(To be continued).

NOTICES OF BOOKS.

Examination of Water (Chemical and Bacteriological). By WILLIAM P. MASON. New York: John Wiley and Sons. London: Chapman and Hall, Ltd. 1899. Pp. v.—135, 12mo. Illustrated.

THE author of this convenient little handbook assumes that the student has a knowledge of ordinary quantitative analysis, and therefore gives mere suggestions for the determination of the mineral matters present in water, and develops more fully items properly lying within the scope of a sanitary examination. In the Introduction Dr. Mason refers to some popular misconceptions concerning the analysis of potable water, and says it should not be looked at from the same point of view as the analysis of an iron ore, because the results reported in the two cases are not analogous, nor equally capable of interpretation. He points out the necessity for the chemist who is analysing a water used for drinking purposes to know its history, its geographical situation, &c. The amount of chlorine found, for example, should be compared with "normal chlorine" of the region whence the sample is taken: this point is illustrated by two maps, one of the State of Massachusetts (prepared by the Board of Health), and one of Connecticut, showing the distribution and quantity of chlorine in the potable waters of the two commonwealths.

The volume gives simple and clear directions for sampling the water to be examined, and for testing its hygienic value. He favours Griess's second method for determining nitrites, the picric acid method of estimating the nitrogen present as nitrates, and Wanklyn's albumenoid ammonia process. Following the description of each analytical process is a paragraph headed with the unusual word "Comparates," which contains sundry data and the opinions of various authorities with reference to the method and the results. This feature will assist the laboratory analyst to make comparisons of the water under examination with others good or bad. A table shows that the rain-water freest from nitric nitrogen falls in the interior of Scotland, and that containing the most in Paris.

The chapter on bacteriological examination is rudi-

* Kruss and Schmidt, *Zeit. Anorg. Chem.*, li., 249; Winkler, *Zeit. Anorg Chem.*, iv., 17. Krüss observed the appearance of a pale rose-coloured flame during the ignition of his nickel in a Rose crucible in hydrogen, accompanied with a loss of weight. If the hydrogen was *dry*, and especially if, as is often the case, it contained traces of hydrochloric acid, minute traces of nickelous chloride might have been sublimed and have caused this phenomenon, which Krüss ascribed to "gnomium" and Winkler ascribed to potassium. This question is worthy of further attention.

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mentary, no attempt being made at ultimate differentiation; Miquel is often cited as authority. Instructions are given for counting the colonies of bacteria and testing for *B. coli communis*.

It is interesting to note that bacteria have been exposed for several hours to liquid air without destroying them; but if the water is heated under pressure to 115° C. for 45 minutes the bacteria are absolutely destroyed. Ordinary boiling of water for half an hour will destroy 99 per cent of the bacteria.

The book has an Index. H. C. B.

Manual of Clinical Chemistry. By ELIAS H. BARTLEY. Philadelphia: P. Blakiston's Son and Co., 1012, Walnut Street. 1899. Pp. vi.—150. 12mo. Thirty-three Illustrations. Cloth.

THE author of this little manual holds degrees and offices that indicate some of his qualifications for instruction in the subject of which it treats; he is "B.S., M.D., Ph.G., Professor of Chemistry and Toxicology in the Long Island College Hospital; Dean and Professor of Organic Chemistry in the Brooklyn College of Pharmacy." His "Text-book of Medical and Pharmaceutical Chemistry," now in its fifth edition, is widely and favourably known to students in Medical Colleges, pharmaceutists, and physicians; the work under review is made up of the last eighty-three pages of that "Text-book," to which have been added notes on urinary diagnosis, and a collection of well-selected experiments with carbohydrates, fats, proteids, and milk, together with a scheme for the qualitative analysis of commercial prepared foods.

The book contains the essentials of a course of laboratory work for the second year of study in most American Medical Colleges, at the same time it supplies physicians with a small handbook on chemical diagnosis as applied to the gastric contents, milk, fæces, and urine. The author acknowledges his indebtedness to Halliburton's "Essentials of Chemical Physiology," in preparing the course of experimental study of the proximate principle of foods.

The book can hardly be used without the "Text-book" containing descriptive chemistry; it opens with the experimental study of carbohydrates, fats, proteids, the albumenoids, milk, and saliva, the directions being concise, and assuming knowledge of elementary chemistry. More than half of the book is given to the study of urine, but the author does not undertake to teach physiology.

Tables of weights and measures, with an Index, close a compact, well-made handbook.

CORRESPONDENCE.

ANALYSIS OF THE ASH OF CARDAMOMS.

To the Editor of the Chemical News.

SIR,—In reference to Mr. H. B. Yardley's report on the ash of cardamoms, I was struck with the remark that "it was of a grey colour, probably due to a small quantity of carbon." And, further, on examining his analysis he made no mention of manganese. It is one of the characteristic features of zingiberaceous plants that most of them take manganese from the soil, and I am of opinion that, if Mr. Yardley repeats his work, he will find that the grey colour is due to manganese. Here is a copy of some analyses done by me not long ago on undoubted specimens of *Elettaria cardamomum*:—

Seeds (whole)	3·26	per cent of ash.
Seeds (crushed)	3·52	,, ,,
Pericarp of fruit	6·17	,, ,,
Pericarp of fruit	5·96	,, ,,
Entire fruit and seeds (six taken in each case) ..	3·8	,, ,,
	4·219	,, ,,

The ash in all cases contained an appreciable quantity of manganese. There are several reports on the ash of cardamoms, some giving as much as 15 per cent; but I am afraid that such an amount is far too high. There are so many varieties of cardamoms that it is just possible that there may be a wide variation in some species. I am, &c.,

W. WATSON WILL.

Metropolitan College of Pharmacy, 162, Kennington Park Road, S.E.

THE NEW YORK PUBLIC LIBRARY ASTOR, LENOX AND TILDEN FOUNDATIONS.

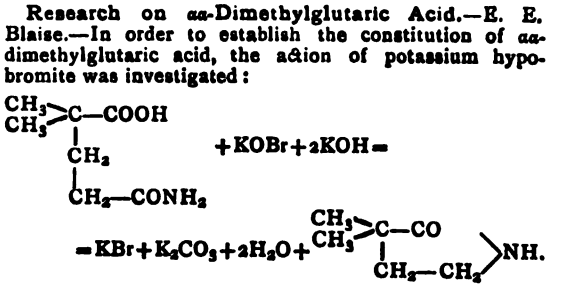
CHEMICAL NOTICES FROM FOREIGN SOURCES.

NOTE.—All degrees of temperature are Centigrade unless otherwise expressed.

Comptes Rendus Hebdomadaires des Séances, de l'Académie des Sciences. Vol. cxxviii., No. 11, March 13, 1899.

Double Cyanides.—M. Berthelot.—The double cyanides selected for experiment were combinations of potassium cyanide with those of zinc, mercury, and silver. The author classifies his research under three heads:—(1). The first part deals with the equilibrium between hydrocyanic acid and acids united with alkaline bases. Strong acids, *e.g.*, HCl and HNO_3, completely decomposed potassium cyanide, with evolution of heat. With weak acids, *e.g.*, C_6H_5OH, the base divided itself between the two acids, the hydrocyanic acid taking three-fifths of the base, for potassium phenolate is dissociated to a greater extent than the cyanide, though, at the same time, the heat of neutralisation of hydrocyanic acid is less than half that of phenol. In the case of weak, polybasic acids, such as H_2S, the results depended on the relative masses. Hydrocyanic acid gave no thermal reaction with alkaline sulphydrates. Boric and hydrocyanic acids shared the alkaline bases, the division depending on the relative proportions. (2). The second part deals with the heat of formation and constitution of double cyanides. On treating a solution of the double cyanide of silver and potassium with a strong acid silver cyanide was precipitated and the potassium cyanide decomposed. With weaker acids (acetic, boric, carbonic, &c.) the phenomena observed indicated the existence of a complex acid, argentohydrocyanic acid, analogous to ferrohydrocyanic acid. For example, carbonic acid produced no effect on the solution of the double cyanide, whilst arsenious and boric acids gave a slight crystalline deposit after some weeks. Acetic acid caused partial precipitation of silver cyanide. The results obtained on operating with the double cyanide of mercury and potassium are comparable with the above, showing that mercurohydrocyanic acid is less stable than argentohydrocyanic acid. In the case of zinc there were also indications of the existence of a zincohydrocyanic acid. The third part of the research, dealing with the action of hydrogen and alkaline sulphides on double cyanides, is not given.

Research on *aa*-Dimethylglutaric Acid.—E. E. Blaise.—In order to establish the constitution of *aa*-dimethylglutaric acid, the action of potassium hypobromite was investigated:



The esterification of the acid was also investigated. As a result, a great difference was found to exist between the two carboxyls.

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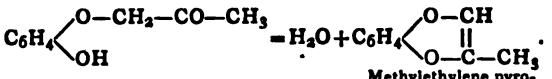
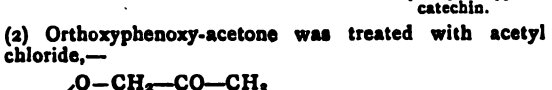
Methylethylene Pyrocatechin.—Ch. Moureu.—This body is the second member of the series of compounds containing a benzene nucleus and a non-saturated dioxy-radicle. It has been prepared from orthoxyphenoxy-acetone by two methods:—(1) Orthoxyphenoxy-acetone was dehydrated by means of phosphoric anhydride in presence of quinoline,—



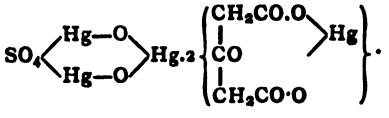
Methylethylene pyrocatechin.

(2) Orthoxyphenoxy-acetone was treated with acetyl chloride,—



Double Iodides of Manganese Dioxide.—A. Berg.—Few compounds are known in which manganese dioxide reacts as a basic oxide, and these are only stable in presence of an excess of acid. The author has discovered that iodic acid gives an iodate of manganese dioxide having properties analogous to those of the other salts of the same nature. Hydrated manganese dioxide was prepared by the action of potassium permanganate on a manganous salt, and this partially dissolved on boiling with a solution of iodic acid, giving a brown solution. It was not possible to isolate the iodate from the excess of iodic acid, on account of its instability; but in presence of certain metallic iodates more stable double iodates were produced. These compounds are insoluble in water, and not much attacked by it. The potassium salt had the formula $(IO_3)_4Mn.2IO_3K$, and similar results were obtained with the barium and ammonium salts.

Sensitive Reaction of Acetone-di-carbonic Acid.—G. Denigès.—In its capacity as ketone, acetone-di-carbonic acid gives a compound with mercuric sulphate corresponding with the formula—



This compound is insoluble in water, and forms a delicate test for traces of acetone-di-carbonic acid.

MISCELLANEOUS.

Australasian Association for the Advancement of Science.—We have received a copy of the Report of the Seventh Meeting of the Australasian Association for the Advancement of Science, held at Sydney in 1898. The Association is conducted on the same lines as the British Association; the matter is distributed over ten Sections, designated by letters A to J, the work in each Section commencing with an Address by its President. In the Presidential Address by Prof. A. Liversidge, M.A., LL.D., F.R.S., the aims, objects, and history of the parent Institution, the British Association, are given in detail, and after a brief reference to the working of other similar institutions, a good *résumé* is given of the more recent advances and discoveries in science. From the number and scope of the papers presented in the various Sections, we conclude that the Australasian Society is in a very healthy condition and is doing really good work. Although mostly of local interest, the papers are none the less valuable; we particularly note the interesting papers in Section F (Ethnology and Anthropology). The volume, of 1161 pages, is well arranged and illustrated, and, considering the amount of matter included, we must congratulate the editors upon the promptness with which it has been issued.

MEETINGS FOR THE WEEK.

MONDAY, 10th.—Royal Institution, 5. General Monthly Meeting.
—— Society of Chemical Industry, 8. "The Industrial Technical Treatment of Sherry and of British Colonial Wines," by Dr. J. T. W. Thudichum, F.R.C.P. (Lond.).
TUESDAY, 11th.—Royal Institution, 3. "Zebras and Zebra Hybrids," by Prof. J. Cossar Ewart, M.D., F.R.S.
WEDNESDAY, 12th.—Society of Arts, 8. "Telephones," by John Gavey, Assistant Engineer-in-Chief and Electrician, G.P.O.
THURSDAY, 13th.—Royal Institution, 3. "The Atmosphere," by Prof. Dewar, M.A., LL.D., F.R.S.
FRIDAY, 14th.—Royal Institution, 9. "Earth Currents and Electric Traction," by Prof. A. W. Rücker, M.A., D.Sc., &c.
SATURDAY, 15th.—Royal Institution, 3. "Machiavelli," by Louis Dyer, M.A.

ROYAL INSTITUTION OF GREAT BRITAIN,
ALBEMARLE STREET, PICCADILLY, W.

Professor DEWAR, M.A., LL.D., F.R.S., M.R.I., Fullerian Professor of Chemistry, R.I., will, on THURSDAY next, APRIL 13TH, at Three o'clock, begin a Course of Three Lectures on—
"THE ATMOSPHERE."
Subscription to this Course, Half a Guinea.

Mr. J. G. LORRAIN, M.I.E.E., M.I.M.E, M.S.C.I.,
Fellow of the Chartered Institute of Patent Agents,
NORFOLK HOUSE, NORFOLK STREET, LONDON, W.C.
"PATENTEE'S HANDBOOK" Post Free on application.

CHEMIST-ENGINEER.
Swiss, with highest references, graduated, knowing the English language, at present in an English Colony, with several years' experience in one of the largest Aniline Colour Works of the Continent, wants Situation in similar Works.—Address, "Z.L. 2111," care of Rudolf Mosse, Zürich, Switzerland.

Young Man desires to enter a good Firm of Analytical Chemists as Junior Assistant. Time given in lieu of wages.—Address. E. E., 5, Jerningham Road, New Cross, S.E.

Junior Assistant wanted in Laboratory, London.—Address, J. A., CHEMICAL NEWS Office, 6 & 7, Creed Lane, Ludgate Hill, London, E.C.

Wanted, Post at home or abroad as Manager or Chemist; scientific training; good experience in the manufacture of B.O.V., R.O.V., Saltcake, Bleaching Powder, Caustic Soda, Nitric Acid, Dyers' Solutions, &c. Full particulars on application.—Address, M. C., CHEMICAL NEWS Office, 6 & 7, Creed Lane, Ludgate Hill, London, E.C.

Wanted, an Analytical Chemist of exceptionally high and proved ability and accuracy, with good experience in testing Medicinal Chemicals, to take up the position of Chief Analyst at the Works of a leading London Firm of Manufacturing Chemists. A gentleman who has taken University Degrees preferred.—Address, stating age, qualifications, and experience, to "Analyst," care of Messrs. Markby, Stewart, and Co., Solicitors, 57, Coleman Street, London, E.C.

Wanted, at a Colonial Government Laboratory in the West Indies, a Chemist holding University Honours Degree to assist in Analysis and Research. Likely applicants will be furnished with full particulars.—Apply, stating age, whether married or single, and qualifications, to D. D., CHEMICAL NEWS Office, 6 & 7, Creed Lane, Ludgate Hill, London, E.C.

WELDON APPARATUS, Second-hand, wanted in thoroughly good working order and condition.—Address, Box 3756, Sell's Advertising Offices, Fleet Street, London, E.C.

FOR SALE.—One Assay and one Chemical Balance, both by Oertling; also two 15 inch diam. Assay Furnaces.—Apply, Messrs. Corbin & Greener, 85, Gresham Street, E.C.

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THE CHEMICAL NEWS.

Vol. LXXIX., No. 2055.

THE NEW YORK PUBLIC LIBRARY ASTOR, LENOX AND TILDEN FOUNDATIONS.

THE ESTIMATION OF CARBON IN STEEL: APPARATUS AND MATERIALS.

The pneumatic stirring apparatus (Chemical News, lxxiv., 63), by means of which any number of samples of steel may be kept constantly agitated, has recently been modified in an important detail by H. Jervis (Chem. News, lxxix., 86). He proposes an additional piece of apparatus, one object of which is to prevent any irregularity in the working of the filter-pump causing the solution to be forced from one flask into another. The means proposed are admittedly inefficient when more than a certain number of flasks are attached to each other. I propose to show why the arrangement must fail ultimately, and to mention a precaution more than sufficient to cover the danger of as many attached flasks as the pump can agitate.

Mr. Jervis's apparatus, however finely it may be adjusted, can avail only when there is an actual backward pressure from the pump. The damage may be done before this point is reached.

Say two flasks are being agitated by a current of air moving in the arrowed direction, and that the foremost one is suddenly detached from the pump. The pressure in the flask A is that of the atmosphere, but the pressure in B is less, because the atmosphere must push back the column of liquid in the straight tube passing through B's perforated stopper before it can destroy the partial vacuum which existed before the pump was detached. But the straight tube passing through A's perforated stopper is in direct contact with the inside of B, and consequently the copper solution must rise in it when flask A is exposed to the normal pressure of the atmosphere.

A moment's reflection will show that the height to which the solution will rise in A's tube depends upon the depth B's corresponding tube dips below the surface, or, similarly, on the number of flasks following A whose tubes dip a certain distance below the surface of their solution. It is thus apparent that with no actual back pressure whatever, and notwithstanding the previously described arrangement, the solution of the first flask may pass into the second.

On the other hand, it should be noticed that the solution of flask B could not, under like circumstances, pass into a following one, C. The pressure in B's straight tube is the same as that of C's flask, and from previous considerations it is plain that the pressure in any flask (except A) is less than than that of any succeeding one, so that the solution of B could never pass into C, or C into D, and so on, unless the straight tubes were *very* short in comparison with the total column of liquid through which the air is drawn: such considerations have nothing to do with the present case.

Obviously the remedy lies in making it very difficult for the solution to pass from A into B, either by making A's straight tube very long or by using a heavy liquid in a flask permanently placed first in a series. The latter is the more convenient device, all that is needed being a small alteration of the Woulf bottle shown in the figured arrangement on page 86. Through each neck of the bottle a tube should pass. One, very narrow, dipping below a layer of mercury, is attached to the dissolving flask; the other, not reaching the surface of the mercury, is attached to the pump. The solution of A can now pass into B only after considerable mercury has been pushed over into A; but as the narrow tube can be made any length, the chances of this taking place may be made as remote as may be wished. It is, of course, just as necessary as ever to detach a long series the hindmost first.

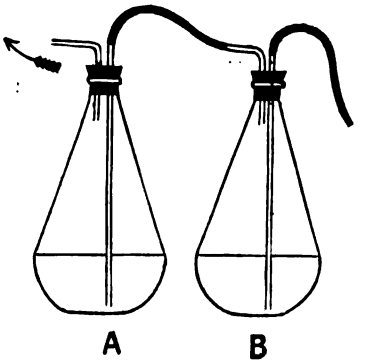
The dissolving of iron in copper solutions is usually expressed by the following equations:—

1. $Fe + CuCl_2 = Cu + FeCl_2$.
2. $Cu + CuCl_2 = Cu_2Cl_2$.

The ammonium, sodium, or potassium chloride is present chiefly for the purpose of retaining the cuprous chloride in solution.

The green copper solution begins to darken almost immediately it is brought in contact with the iron. This shows, if the operation is substantially represented by the above equations, that the second reaction follows close on the heels of the first. This must be so, because it is to the reaction between the copper and the copper ammonium chloride that the blackening is due, or, more strictly speaking, to the fact that this operation forms the cuprous in the presence of cupric chloride.

On dissolving metallic copper in an acid solution of copper ammonium chloride, the colour changes are:—Bright green, olive-green, light brown (black in the mass), dark brown, and then—if the copper is in excess—reddish brown, to a practically colourless solution of cuprous chloride. This solution, dropped into copper ammonium chloride, produces a black cloud, and we can thus exactly simulate the colour changes which attend the dissolving of an ordinary sample of steel. A mixture of no other of the compounds formed so satisfactorily explains the darkening of the solution.



The new compounds formed by dissolving a sample of steel are cuprous chloride and ferrous chloride. Both these bodies oxidise readily in the air, so that when the solutions are pneumatically agitated they become partially re-oxidised. By continuing to pass the air the oxidation is nearly completed, and the solution regains its original green colour.

The question very naturally arises as to whether such a solution can be advantageously re-used, and, if so, how often?

Three hundred c.c. of a saturated solution of copper ammonium chloride was agitated with 5 grms. of steel. Keeping the filtrates at about 300 c.c. by occasional evaporation, successive lots of 5 grms. each were dissolved and filtered. The original solution contained 5 per cent strong HCl, and more acid was added as required, in order to form the chloride of the increasing amounts of iron. After this operation had been repeated four or five times, there was a decided decrease of the rate at which the solution could be filtered. The filtration of the seventh sample was decidedly slow, and that of the eighth impossible without previous dilution. Before the eighth sample was dissolved, crystals separated; not crystals of an iron salt, as I had hoped, but crystals of copper salt. Had the iron crystallised out, a theoretically unending use of the same solution would have been possible.

The carbonaceous residue of the first six samples, with

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no other precautions than attach to every-day technical estimations, were combusted. The results were:—

I.	.. .. ..	1·21 carbon per cent.
II.	.. .. ..	1·19 ,, ,,
III.	.. .. ..	1·18 ,, ,,
IV.	.. .. ..	1·20 ,, ,,
V.	.. .. ..	1·20 ,, ,,
VI.	.. .. ..	1·19 ,, ,,

In another case the samples were successively added without filtering off the the separate carbonaceous residues. Here, as before, the sixth, seventh, and eighth samples were dissolved much slower than the first three or four samples. The combustion of the total residue of the 40 grms. of steel used gave 1·16 per cent carbon.

From these experiments it is apparent that, after dissolving one sample, the copper ammonium chloride need not be regarded as useless.* It may be used three or four times where the convenient practice is adopted of allowing the sample to be dissolved during the night.

Neutral copper solutions cannot be so conveniently used with the pneumatic stirrer, because the iron after oxidation is thrown out and messes the flask and tubes. If, however, the sample be dissolved by shaking in a stoppered flask, the solution may be filtered without any appreciable amount of iron being thrown out. The filtrate can then be oxidised by the air current, the iron oxide allowed to settle, and the clear green solution re-used. Theoretically there is no limit to the number of times a solution may be used in this way. The following are the results of four carefully combusted residues obtained by the successive use of the same solution:—

I.	.. .. ..	1·184 carbon per cent.
II.	.. .. ..	1·184 ,, ,,
III.	.. .. ..	1·178 ,, ,,
IV.	.. .. ..	1·184 ,, ,,

J. T.

THE PRECIPITATION OF CADMIUM BY SULPHURETTED HYDROGEN.

By ROBERT MELDRUM, F.C.S.

In the qualitative examination of solutions for cadmium, it is usual to acidify with HCl, heat, and pass H_2S gas through same. HCl is not the most reliable agent for this purpose, as will be seen from the following table. Column I. = grms. $CdSO_4.xH_2O$ in 10 c.c. of H_2O precipitated in cold by H_2S gas. Columns II. and III. = c.c. of strong HCl required to dissolve precipitate to a colourless solution.

I.	II. At 10° C.	III. At 100° C.
0·050	3·0	1·0
0·045	4·0	0·9
0·040	3·5	0·8
0·035	3·5	0·9
0·030	3·0	0·8
0·025	3·0	0·8
0·020	2·5	0·8
0·015	2·5	0·6
0·010	2·0	0·5
0·005	1·5	0·4
0·0025	1·5	0·3

Several cases of failure to discover cadmium when present in appreciable quantity have of late come under my notice, and I have no doubt that this is due to excess of HCl being present. Acetic and sulphuric acids have little or no solvent action on the precipitated sulphide, even when present in excessive proportion. Cases will occur where the solution contains excess of chlorides of the metals decomposable by H_2S with liberation of HCl, and it is especially here where small quantities are liable to escape detection.

Neutral solutions containing from 0·025 to 0·05 grm. $CdSO_4.xH_2O$ or more per 10 c.c., when precipitated in the cold by H_2S gas, give a canary-yellow curdy precipitate, which settles in a few minutes, leaving a dense opaque yellow solution above. Heated to boiling, the precipitate changes to orange-yellow, settling rapidly and leaving the liquid clear with a slight yellow tinge. As the solution cools, the orange-coloured precipitate becomes—to a slight extent—paler, but does not regain its former colour. If the hot solution be agitated while cooling, and when thoroughly cold, the precipitate settles slowly, leaving an opaque solution above. From these properties alone, it is possible to distinguish the yellow precipitate of cadmium sulphide from all other precipitates, and seem to me to be very characteristic.

In solutions containing from 0·02 to 0·005 grm. of the cadmium salt per 10 c.c. a precipitate falls in a few minutes, leaving a yellowish opalescent solution above. All change to dark yellow on boiling, but do not clear rapidly, remaining somewhat milky.

In solutions containing from 0·0025 to 0·002 grm. of cadmium salt per 10 c.c. a strong yellow opalescent solution results from which no precipitate settles out in thirty minutes. On boiling, a small precipitate settles out from each, leaving the solution faintly yellow.

0·00175 grm. in 10 c.c. gives opalescent solution of a strong yellow colour, yielding no precipitate on standing for one hour or on boiling.

0·00125 to 0·0015 grm. in 10 c.c.: faintly opalescent solution, from which no precipitate settles out in one hour. 0·001 to 0·00075: very distinctly yellow solution. 0·0005: in 2-inch column distinctly yellow. 0·000125: no colour in 2-inch column.

All the above are only apparently yellow solutions, as on standing for twenty-four hours, the sulphide—which appears to exist in the colloidal state—undergoes a change to the amorphous condition, and falls to the bottom as a yellow precipitate, leaving the solution of a faintly yellow tint. In all precipitations of cadmium in neutral solutions by H_2S, the greater part of the sulphide is in the amorphous state, a very small part in the colloidal state, and—as we shall presently see—a still smaller proportion in the soluble state. Solutions of cadmium containing more than 0·0175 per cent of the salt, when precipitated by H_2S gas, yield a filtrate almost free from colour in 2-inch columns; whereas, should the Cd be present in lesser quantity than this, the filtrate is always highly coloured. Thus:—

0·025 per cent.	No colour in 2-inch column of filtrate.
0·015 ,,	Faint trace of colour in 2-inch column of filtrate.
0·0125 ,,	Colour of filtrate very distinct.
0·010 ,,	Filtrate highly coloured.
0·0075 ,,	,, ,,
0·005 ,,	,, ,,

Solutions containing from 0·0175 to 0·015 per cent of salt, when re-filtered several times through the same paper, the filtrate is latterly as colourless as water. Weaker precipitated solutions than these may be re-filtered over and over again without any appreciable decrease in colour, thus indicating that the cadmium in these cases exists in the soluble condition. If these filtered solutions are allowed to stand over twenty-four hours, a small precipitate always settles out, the solution still retaining a faint yellow colour.

To account for strong precipitated solutions of cadmium yielding an almost colourless filtrate, and weaker solutions a coloured one, two explanations present themselves.

* I know that in some laboratories the practice of a system of fractional crystallisation enables the bulk of the iron to be concentrated in a volume of mother-liquor some five or six times less than the original volume of the filtrates, and provides also crops of crystals of more or less pure copper ammonium chloride, which may be used for dissolving steels.

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(1) In the case of strong solutions, the large curdy precipitate entangles the colloidal and soluble sulphides and carry them down, in the same way that any other bulky precipitate would carry down other gelatinous and soluble matter when present in small proportion. (2) That the large precipitate forms a film on the paper preventing the passage of both the soluble and colloidal forms.

I find that cadmium under a great many circumstances may be accurately estimated by a colorimetric method based upon the above properties when the amount of Cd present does not exceed 0·02 per cent $CdSO_4.xH_2O$.

THE DETERMINATION OF ARSENIC IN GLYCERIN.

By A. C. LANGMUIR.

THE presence of arsenic in glycerin is probably by this time well known to chemists. Several have described its detection qualitatively. Barton (*Journ. Amer. Chem. Soc.*, xvii., 883), however, was the first to estimate it quantitatively. Barton's method, which was applied on C.P. glycerins only, consists in the charring of 5 grms. of the glycerin with sulphuric and nitric acids, the production of a mirror in the Marsh apparatus, and the comparison of the mirror so obtained with a standard mirror according to Sanger's method (*Proc. Am. Acad. Sci.*, 1891, xxvi., 24).

As it is impossible to draw an accurate comparison if the mirrors weigh over 0·06 milligrm., a suitable aliquot part of the solution must be taken, in order to obtain a mirror weighing less than this amount. This requires some experimenting on the part of the analyst, which becomes very tedious if the glycerin be high in arsenic.

These considerations led the author to abandon the method and adopt a modification of Polenske's process (*Chem. Centrbl.*, 1889, lx., [2], lviii.), suitable to the case at hand. The method as described by Polenske is accurate with quantities of arsenic up to 4 to 5 milligrms. As in glycerin analysis the amount of arsenic in the portion taken rarely exceeds 1 milligrm., the apparatus may be materially simplified.

For analysis we take 15 to 20 grms. of a crude soap lye glycerin and 25 to 30 grms. of a saponification or C. P. glycerin. With dilute glycerins an amount is taken which would yield the requisite weight upon evaporation. The weighed sample is made up to 100 c.c. with hot water and rinsed into a capacious casserole, containing a mixture of 200 c.c. of concentrated nitric acid, and 12 c.c. concentrated sulphuric acid. Cover and heat gently in the hood until the action starts. Remove the flame and wait until the violence of the reaction is over, then boil down slowly over a low flame until dense fumes of sulphuric acid appear. Raise the heat at the end to expel the last traces of nitric acid. If the concentration has been a slow one (four to five hours) the organic matter will generally be entirely oxidised. If the acid turns brown, however, from the charring of organic matter, it is well to boil for some time longer to complete the oxidation. There is no danger of losing any arsenic by this treatment. Cool and dilute to 50 c.c.

About 40 grms. of coarsely granulated zinc are placed in the generating flask of the Marsh apparatus. A 75 to 100 c.c. stop-cock funnel pierces the stopper. The escaping gas is passed through a wash-bottle containing a 5 per cent lead nitrate solution to remove any hydrogen sulphide, and is dried by passing through a calcium chloride tube. A tube of hard glass about 10 inches long and with an inside diameter of 10 to 12 m.m., is heated near one end and drawn out at that point to a tube with a diameter of 1 to 1½ m.m. This section serves to catch the metallic arsenic deposited. Of the large sections the longer is heated by two Bunsen burners. To prevent sagging it is well to protect this part of the tube with a roll of copper gauze wrapped around it. The shorter section at the end of the tube holds a slip of filter-paper moistened with a saturated solution of mercuric chloride. This serves to detect the presence of any hydrogen arsenide which might pass the burners undecomposed.

After making connections 10 c.c. of 20 per cent sulphuric acid is run into the flask. When the air has been entirely displaced rinse the solution to be tested into the stop-cock funnel, light the burners and run the solution, drop by drop, on the size at such a rate that not more than two bubbles a second pass the lead nitrate wash-bottle.

If the mercuric chloride paper should at any time show a yellowish tint the solution should be run in more slowly. If the size of the mirror shows that a considerable amount of arsenic is present, it is well to add, at the end, a little stannous chloride dissolved in hydrochloric acid. In any case add a few cubic centimetres of dilute acid after the entire solution has been run in to expel hydrogen arsenide remaining in the flask.

The section carrying the mirror is separated by a file and carefully weighed on an assay gold balance within 0·01 milligrm. This can be readily done, as the weight of the tube seldom exceeds 300 milligrms. The arsenic is dissolved by dipping the tube into hot dilute nitric acid, and after washing and drying the weight is taken again, the difference being the weight of the arsenic forming the mirror. The zinc and acids used should not form a perceptible mirror after running the apparatus three quarters of an hour. The following results were obtained:—

Arsenic taken. Milligrms.	Arsenic found. Milligrms.
0·20	0·17
0·50	0·45
0·75	0·68

Several C. P. glycerins were found to be free from arsenic. Arsenic was found in a majority of saponification glycerins. These averaged about 0·00018 to 0·00030 per cent. A number of crude soap-lye glycerins gave percentages lying between 0·00064 and 0·01.

A very fair idea of the arsenic contents may be gained by Gutzeit's test, using mercuric chloride instead of silver nitrate. Two c.c. of glycerin are run into a five-inch test-tube and diluted with 4 c.c. of water; a piece of granulated zinc is added and sufficient hydrochloric acid to just start the reaction. The tube is then quickly closed by a cork whose lower end is covered with a 7 c.m. filter-paper. The paper is wrapped around the cork so that it rests smoothly against the lower end. This part is moistened with two drops of a saturated solution of mercuric chloride. The hydrogen escapes through the creases between the paper and the tube. The evolution of hydrogen should be fairly brisk but not too violent.

After standing ten minutes the cork and paper are removed. The latter is spread out and examined. A yellow stain in the shape of a circle with a diameter equal to the end of the cork is formed if arsenic were present. With very impure glycerins the colour is brown. The papers carrying the stains may be marked and kept as records for future comparisons. The colour is fairly permanent. By comparing the yellow stain produced by the glycerin under examination with a series of standards prepared by running the same test on portions of a solution of arsenic (1 milligrm. in 100 c.c.). the per cent of arsenic can be gauged quite accurately after a little practice. The colour is quite distinct with 0·01 milligrm. of arsenic and is still perceptible with 0·0025 milligrm. If the latter amount were present in 2 c.c. glycerin (sp. gr. 1·26) the per cent of arsenic present would be 0·00010, which would be about the limit of delicacy by this test.

Gutzeit's test using silver nitrate was found to be very unsatisfactory. It is very difficult to form any idea as to the amount of arsenic present from the intensity of the colour in this case. The silver nitrate is also so easily affected by impurities in the zinc and acid other than

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arsenic that any conclusion as to the presence of the latter should be drawn with great caution.

In view of the rapidity, delicacy, and accuracy of Gutzeit's test, using mercuric chloride, it is difficult to understand why the more laborious Marsh test should still hold its own as a qualitative test for arsenic.—*Journal of the American Chemical Society*, xxi., No. 2.

ON THE ACTION OF ALUMINIUM AS A REDUCING AGENT.

By L. FRANCK.

The Action of Aluminium on Compounds of Phosphorus.—The vapour of phosphorus when caused to impinge on powdered aluminium, heated to a dull red in a current of hydrogen, combines with this metal with incandescence. An agglomerated mass is formed, of a blackish-grey colour, which decomposes on contact with moist air, giving PH_3 and leaving a greyish-white residue. Water also decomposes this body, giving a hydrate of alumina and a brown residue. It is again decomposed by acids and alkalis, which dissolve it almost completely, giving off phosphoretted hydrogen. Heated in air this compound remains unchanged.

At more or less elevated temperatures all the derivatives of phosphoric acid (meta-, ortho-, and pyro-salts) are decomposed by aluminium. But it is the metaphosphates which undergo the most complete transformation. The reaction is represented by the equation—

$$6NaPO_3+15Al=6NaAlO_2+2Al_2O_3+Al_5P_3+P_3.$$

By adding silica the reaction becomes—

$$6NaPO_3+10Al+3SiO_2=3Na_2SiO_3+5Al_2O_3+3P_2.$$

The salts of calcium or magnesium are as efficacious as those of sodium, but commercial superphosphates cannot be made to serve for the preparation of phosphorus by this method. On the contrary, we obtain excellent results by using the ash of bones decomposed by hydrochloric instead of sulphuric acid.

In this manner phosphorus can be prepared with almost quantitative results, at relatively low temperatures.

The Action of Aluminium on Carbon Compounds.

1. *On Carbonic Acid.*—When dry carbonic acid is passed over powdered aluminium heated to redness, the temperature rises rapidly, owing to the reaction which is developed. On allowing the product of this reaction to cool in carbonic acid, we notice that alumina and amorphous carbon are formed; but if we treat this with hydrochloric acid, a gas with a disagreeable odour is given off, indicating that carbide of aluminium has been formed. The reaction corresponds exactly to the equation $3CO_2+4Al=2Al_2O_3+3C$.

2. *On Carbonic Oxide.*—We obtain the same results as in the preceding case. The reaction is as follows:—$3CO+2Al=Al_2O_3+3C$. As in the case of carbonic acid, a little carbide of aluminium is formed.

3. *On the Carbonates.*—A mixture of an alkaline carbonate with metallic aluminium, prepared in proportions corresponding to the equation—

$$Na_2CO_3+2Al=Al_2O_3+C+Na_2,$$

and heated to redness, becomes incandescent. The products of the reaction are metallic sodium and amorphous carbon.

The author has succeeded in reducing lithium, sodium, potassium, calcium, barium, and strontium in this manner.

4. *On Carbon.*—The author confirms the opinion of MM. Gunts and Masson, according to which the presence of iodide or chloride of aluminium favours the formation of the carbide when aluminium is heated in carbonic acid or carbonic oxide. Powdered aluminium heated with lampblack appears at first to have undergone no change, but under the action of water it gives off a large quantity of hydrocarbon gas. It is, however, impossible to separate the excess of lampblack. We can obtain a large proportion of carbide of aluminium by the direct combination of these two elements, but pure carbide cannot be prepared except by the aid of the electric furnace.

Action of Aluminium on the Oxides.—The mixture of oxide of copper and aluminium in proportions calculated for the theoretical reduction detonates violently when heated to redness. With a large excess of aluminium a bronze is obtained. The reaction is identical with oxide of silver. Oxide of glucinum is also reduced, but only with incandescence. Lime may also be partially reduced by aluminium, and this process would enable us to prepare alloys of calcium, but this is doubtful. The same applies, but in different degrees, to barium and strontium. Finally, aluminium reduces, more or less easily, the oxides of zinc, cadmium, mercury, lead, boron, silicon, phosphorus, arsenic, iron, manganese, cobalt, nickel, and molybdenum.

These reactions have long been known, and Keller has generalised them in a very complete work ("Contributions to the Study of Reducing Agents," *Moniteur Scientifique*, March, 1896, p. 190).

Action of Aluminium on Sulphates and Chlorides.—The mixture of aluminium with sulphate of baryta (or any other sulphate) detonates when heated. Among the products of the reaction we find finely divided sulphur and sulphides. All the chlorides are reduced by aluminium.

Action of Aluminium on Peroxide of Sodium.—The mixture of these two bodies detonates on heating. By moistening with water it is spontaneously inflammable.—*Chemiker Zeitung*, 1898, p. 236.

ON A CRYSTALLINE BASIC CHLORATE OF COPPER.

By L. BOURGEOIS.

It is well known that the careful decomposition of the neutral nitrate of copper, by the action of heat, readily gives a crystallised basic nitrate, which I have shown (*Comptes Rendus*, 1890, cx., 541) to be identical with gerhardtite, a mineral found in the United States by Messrs. Brush, Penfield, and Wells (*Amer. Journ. Sci.*, [3], 1885, xxx., 59). This same basic nitrate,—

$$4CuO.N_2O_5+3H_2O,$$

occurs either in the orthorhombic form of gerhardtite or in the state of the dimorphous clinorhombic variety, according to circumstances; in every case the neutral nitrate loses nitric acid, as has been shown by several chemists, notably G. Rousseau (*Comptes Rendus*, 1890, cxi., 38), L. Michel (*Bull. Soc. Min.*, 1890, xiii., 139), Atanasesco (*Bull. Soc. Chim.*, 1894, xi., 1112), and myself (*loc. cit.*).

Following quite another line of thought, the works of Mallard (*Bull. Soc. Min.*, 1894, vii., 349—401) have called attention to the isomorphism existing between the nitrates and the chlorates,—a very important fact from the chemical point of view, since it tends to show that the chlorine in the chloric acid should be triatomic or pentatomic. Basing our ideas on these relationships, we may well ask if the neutral chlorate of copper, a salt of which the chemical composition and the properties altogether agree remarkably with those of the nitrate, would not also give a crystallised sub-salt corresponding to gerhardtite.

The existence of a basic chlorate of copper was in 1843 described by Al. Waechter (*Journ. f. Prakt. Chem.*, 1843, xxx., 321; *Journ. de Pharm. et de Chim.*, [3], 1844, v., 360) as resulting from the decomposition of chlorate of copper by the action of a moderate heat; and from the complete

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work of this chemist on the metallic chlorates we gather that, alone among these, chlorate of copper undergoes a decomposition comparable to that of the nitrate. Waechter describes the basic chlorate as being a green body, insoluble in water, very soluble in acids; but he gives no analysis, and does not mention whether there are any indications of crystallisation.

The communication I have the honour of presenting to the Society has for its object to decide whether the green salt of Waechter corresponds chemically and crystallographically with gerhardtite, and to see whether it is as easily formed as this body under practically similar circumstances.

If, for example, we heat in a flask on the sand-bath crystals of chlorate of copper, $(ClO_3)_2Cu+6H_2O$, we observe that they melt at about 65° in their water of crystallisation, giving a blue liquid of a syrupy consistence. The decomposition of the salt commences, though very slowly, at about 100°; towards 110° to 120° it is rapid, without being violent. We then notice that the liquid takes a cloudy deep-blue tint rather inclined to green, and gives off small bubbles of gas (peroxide of chlorine, chlorine, and oxygen), while at the same time continuous decrepitation is heard.

The greater part of these phenomena accompanying the decomposition of the chlorate have been described by Waechter. Soon the basic salt is deposited, and a crystalline appearance is already manifest to the naked eye. When the mass has become sufficiently thick owing to the deposition of crystals, the operation is stopped; after cooling we wash with cold water, which removes the undecomposed neutral chlorate; the crystals are thrown on a filter, washed, and dried.

If, in the same manner, we had carefully heated crystals of nitrate of copper on the sand-bath, but to a slightly higher temperature, we should, as is well known, have obtained gerhardtite. The formation of this body is easily explained; it should be remarked that the nitrate of copper decomposes very distinctly into gerhardtite and nitric acid, $NO_3H+3/2H_2O$; the vapours of this latter condense on the cooler parts of the vessel, fall back on the small vessels which have just been formed, partially dissolving them, and this reversible reciprocal reaction going on continuously enables the crystals to increase in size. It is less easy to account for the production of the crystals of subchlorate of copper, inasmuch as chloric acid is not volatile without decomposition, and the salt is formed during the course of a reaction which is not only not reversible, but even appears to be slightly explosive.

On the other hand, we have proved that the subchlorate of copper dissolves with heat into a very concentrated liquid of neutral chlorate, and that this solubility increases with the temperature and the concentration. Thus we find realised, from the continuous movements which accompany the decomposition of the chlorate, conditions enabling the crystallisation of the basic salt to take place. When we take up the mass with water after cooling, we always get, besides the already formed crystals, a very slight bluish green cloudiness, due to a deposit entirely formed of micro-crystalline basic chlorate. Pressure also varies the speed of decomposition of the chlorate of copper; if we operate *in vacuo* the reaction becomes violent, and only gives an amorphous product (it is the same with the nitrate); in a sealed tube it appears to be retarded, but nevertheless gives off chlorine and oxygen; the dimensions of the crystals, however, do not increase as I had hoped.

The same salt is also formed when we heat a solution of chlorate of copper with fragments of marble, or again with urea, to about 130° in a sealed tube, but the crystals obtained are less voluminous than those furnished by the first process.

Basic chlorate of copper exists in the form of small tablets of a very beautiful green colour, often reaching several tenths of a millimetre, and sometimes even 1 or 2 m.m. in diameter; their density is 3·55. At first sight they resemble gerhardtite, only the tablets of this latter are more jagged and irregular. Further on we shall treat of their crystallographic and optical poroperties. The substance is insoluble in water, but easily soluble in even the weakest and most dilute acids; the well-known reactions of the chlorate can be easily recognised, and it can be easily shown that there is no chlorine present in the state of chloride. On calcination it becomes black, gives off water, chlorine, and oxygen, and leaves a residue of cupric oxide, which, contrary to Waechter's opinion, is not pure, but still retains chlorine in the form of cupric oxychloride or of cuprous chloride.

The salt has been analysed by dissolving it in the cold in water, to which just sufficient nitric acid has been added; the dilute liquid is then saturated with a solution of carbonate of sodium, which is added until all the copper is precipitated. We then boil the liquid for some time, so as to convert the basic carbonate of copper into black oxide, which is collected on a filter and weighed. The filtrate is evaporated to dryness, leaving a residue of chlorate of sodium with a little nitrate and carbonate. This is gradually calcined until it reaches a dull red heat; all the chlorate is then converted into chloride. Take up with water, acidulate with nitric acid, and estimate the chlorine with nitrate of silver. Thus for 100 parts of material we get the following results, which lead to the formula $4CuO.Cl_2O_5+3H_2O$ or $(ClO_3)_2Cu+3Cu(OH)_2$, corresponding to that of gerhardtite:—

	I.	II.	Calculated.
Cupric oxide	60·2	60·0	60·8
Chloric anhydride (theoretical)	—	28·4	28·8

It is now time to try and discover if the chemical analogy shown to exist between our product and gerhardtite exists also crystallographically. A superficial examination would lead us to say Yes; the crystals of the basic chlorate form, in fact, tablets with an irregular hexagonal contour, which might be derived from an orthorhombic prism with the base p predominant, and with facets with zones ph' and pm. The birefrangibility is strong, the extinction of parallel polarised light takes place along the large facets h', the angle mm measured under the microscope as a plane angle is about 94° 30'; now the value of the angle mm of gerhardtite is 94° 50'; there should therefore be isomorphism with this latter. A closer study, however, particularly with regard to its properties with convergent polarised light, leads us to altogether different conclusions. The direction of elongation is positive, and the plane of the optical axes is parallel to the direction of elongation of the faces (which we will call ph'). The flattened face p is very little out of being normal to the obtuse bisector n_p, and makes a small angle with the mean axis of optical elasticity n_m; the acute bisector n_g is contained in the plane of the face parallel to its elongation. These facts can be explained by comparing our basic chlorate not with gerhardtite, but with the dimorphous nitrate of this latter, obtained artificially by Messrs. Penfield and Wells, also by M. Rousseau. We get, in fact, in this last product, which is clinorhombic, for the angle mm measured on the base p, the value 94° 50', happily equal to the di-hedral angle mm in the dimorphous species, and very close to that of the plane angle found in these crystals. On the other hand, they have facets of which the angles with the principal face, p, could be measured with the goniometer on the largest samples, although the images were rather defective: these angles are of 114° 22' and 107° 5'. Now in the dimorphous specimens of gerhardtite we calculate, from the data given by Messrs. Penfield and Wells, that, if the facets $o\dot{1}$ and $b\dot{1}$ existed, we should have $po\dot{1} = 150° 50'$, and $pb\dot{1} = 106° 3'$ These considerations force us to admit that our crystals correspond to the dimorphous clinorhombic variety of gerhardtite, and not to this latter body itself, and that they possess the faces p, $o\dot{1}$, and $b\dot{1}$.

The neutral bromate of copper (prepared by the double

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decomposition between bromate of barium and sulphate of copper) heated gradually at the ordinary pressure, as was done with the chlorates, decomposes more rapidly, giving off oxygen and bromine vapour; the phenomenon goes on, the same as with the chlorate or the nitrate, when heated *in vacuo*. We obtain basic bromate in the form of a very fine greenish blue powder, in which no crystalline form can be recognised even with the highest magnifying powers.—*Bull. Soc. Chim.*, Series 3, vol. xix.-xx., No. 23.

A REVISION OF THE ATOMIC WEIGHT OF NICKEL.*

Second Paper.—The Determination of the Nickel in Nickelous Bromide.

By THEODORE WILLIAM RICHARDS
and
ALLERTON SEWARD CUSHMAN.

(Continued from p. 166).

The question now arises, whence came this nickel? Was it occluded as nickelous bromide in the interior of crystals of sodic bromide, and thus protected from reduction, or was it dissolved as hydroxide from the spongy metal? The large quantity of nickel present seemed to overthrow the former alternative, but the possibility of the latter is emphatically denied by Winkler (*Zeit. Anorg. Chem.*, iv., 12), and rejected after some hesitation by Krüss (*Zeit. Anorg. Chem.*, ii., 238). Since the equivalent of nickelous bromide is very near that of sodic bromide (109·3 : 103), and the impurity was calculated from the amount of bromine present, the point has no important bearing on the immediate problem; but nevertheless it is always interesting to settle a mooted question of this sort.

Winkler's experiments were made with coherent nickel coated on the inside of a platinum dish, while Krüss's experiments were made with spongy metal in porcelain vessels. The former found no trace of any substance in the water in which his nickel had been digested, while the latter found a large residue (most of which must have come from the porcelain), and hastily ascribed this residue to the presence of an unknown element. It is not at all impossible that, in spite of the well-known permanence of the smooth bright surface of a nickel-plated object, the spongy metal reduced by hydrogen might be easily oxidised and dissolved.† The difference in this respect between polished iron and the same metal reduced by hydrogen is well known. Hence Winkler's experiments prove nothing with regard to the behaviour of finely divided nickel. The position of nickel on the positive side of hydrogen in the electro-chemical series leads one to expect that it must behave as zinc and iron do, although to a less degree. (See a paper entitled "Autoxydation," by R. Ihle, *Zeit. Phys. Chem.*, xxii.,[114).

In order to decide the matter so far as the present work is concerned, we sought to determine experimentally, first, if the purest water is capable of acting on the purest nickel, and secondly, if the hydroxide thus formed is slightly soluble in water. To settle the first point, some very pure reduced nickel was thoroughly washed with water, and then digested at 20° for some time with repeated portions of water just purified. In every case nickel could be found in the filtrate, both by means of potassic thiocarbonate and by evaporation to dryness. Many repetitions of the experiment with new samples of metal brought always the same result. It is quite possible that galvanic action hastened this oxidation, for of course the nickel was contained in a platinum dish. Since Winkler's dish was evenly coated, the water probably did not touch the platinum in his case, and hence this possible cause of acceleration was absent; but the difference between the smooth surface and the finely divided surface alone is amply sufficient to explain the difference in the speed of the reaction.

It will be remembered that Krüss, in one of his experiments, digested a mass of nickel for a year on the steam bath with water, and obtained a white residue which was the chief basis of his alleged discovery. Our work shows that this residue must have contained not only dissolved porcelain, but also enough nickel to yield the black sulphide, the pale green colour, and the electrolysed metal which led Krüss so far astray.

It is clear that, since no acid was present in the water, *the nickel must have been dissolved in the form of hydroxide*. In none of our experiments with the purest metal did the solution give an alkaline reaction with phenolphthalein; hence hydroxyl ions must be absent, and the hydroxide must be dissolved in a colloidal form. The alkaline reaction sometimes observed by Krüss and Winkler must have been due to impurities, as Winkler pertinently suggests. Traces of alkali would surely be found in nickel oxide precipitated in glass vessels, even when mercuric oxide was used as the precipitant.

Nickelous hydroxide, precipitated by alkali and thoroughly washed, possesses at least as great solubility as the hydroxide which is formed by the slow oxidation of nickel. Upon suitable electrolysis, 15 c.c. of such a *cold* solution yielded 0·00062 grm. of nickel, while another similar portion yielded 0·00057 grm., or about 0·04 grm. per litre. Since the solubility is a colloidal one, its limit is indeterminate; hence no elaborate attempt was made to discover its exact amount. It is well known that the presence of other salts in the solution diminish this kind of solubility, but the small amount of sodic bromide present in this case was insufficient to produce any considerable effect. Undoubtedly the fact that the solubility is colloidal and uncertain is responsible for the conflicting statements of the various authorities and handbooks.

(Finkener, "Handbuch der Anal. Chem. von Rose, 6te Auflage von Finkener," ii., 136; Busse, *Zeit. Anal. Chem.*, xvii., 60; Fresenius, "Quant. Anal.," 1877-1887, ii., 393, 823; Roscoe and Schorlemmer, "A Treatise on Chemistry," vol. ii., Part 2, p. 149; Winkler, *loc. cit.*; Krüss, *loc. cit.*; &c. Temperature is a circumstance which produces great effect on this kind of solubility, heat being apt to coagulate the dissolved material).

This solubility of nickelous hydrate is the circumstance which obliged us to determine the residue of sodic bromide through argentic bromide, instead of simply by evaporating the wash-waters poured off from the nickel and weighing the residue. This necessity is made clear by the following table:—

No. of Anal.	Weight of nickel.	Weight of residue extracted by water and dried at 105° C.	Weight of AgBr.	Weight of NaBr calculated from AgBr.	Weight unaccounted for.
	Grm.	Grm.	Grm.	Grm.	Grm.
6.	0·805	0·00330	0·00410	0·00225	0·00105
7.	1·488	0·00895	0·01398	0·00767	0·00128
8.	0·607	0·00400	0·00568	0·00311	0·00089

In order to prove that this large percentage of unexplained residue consisted chiefly of nickelous hydrate, two more determinations were made with new material. Since enough data for the atomic weight had been obtained, and time pressed, the bromide of nickel was not weighed in the first place. In these analyses the *nickel* dissolved as hydroxide was also weighed.

* Contributions from the Chemical Laboratory of Harvard College. From the *Proceedings of the American Academy of Arts and Sciences*, vol. xxxiv., No 13, February, 1899.

† It is a peculiar household fact that cold water faucets plated with nickel are usually less brilliant than their hot water comrades; this difference may well be ascribed to the slow action of condensed water, even upon polished nickel. The greater tendency to rust shown by cobalt may well be due to the fact that in its case the hydroxide is converted into a higher state of oxidation immediately upon being dissolved, thus giving opportunity for the solution and hence for the formation of more hydroxide. In the case of nickel the thin permanent film of $Ni(OH)_2$ probably protects the metal, although its solubility may be no less than that of $CO(OH)_2$.

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	Grm.	Grm.
Weight of residue obtained, dried at 105°	0·00925	0·00480
Argentic bromide found	0·01405	0·00630
Nickel deposited electrolytically ..	0·00092	0·00084
Sodic bromide calculated	0·00770	0·00345
Nickelous hydroxide calculated ..	0·00146	0·00133
Total calculated weight of residue..	0·00916	0·00478
Weight unaccounted for	0·00009	0·00002

Besides this quantitative proof that the residue consisted of nothing but sodic bromide and nickelous hydrate, many qualitative analyses had shown the absence of lime, alumina, silica, and even potash, from the solution poured off from the reduced nickel. Traces of sulphuric acid were found, as has been said, only in the first specimens.

In the light of all these results, no doubt seemed to remain as to the proper mode of correcting the direct gravimetric results of the reduction. Obviously the weight of the sodic bromide must be subtracted from the weights of both the nickelous bromide and the metal formed from it by the action of the hydrogen; for the salt existed in each. On the other hand, the nickelous hydroxide was simply to be neglected; for this substance was formed after the last weighing had been finished. The temperature used for the reduction was so low that no sodic bromide was vaporised; at least none could be found in the cooler parts of the reduction tube.

Analyses 5 and 6 were made with nickelous bromide of the grade of purity represented by the numeral II. in the former paper, while all the others were made with that labelled III., which had been made through the carbonic oxide process. The headings of the various columns will show with sufficient clearness the meanings of the figures given in the accompanying table.

The Atomic Weight of Nickel.

FOURTH SERIES.—O = 16. Ratio = $NiBr_2$: Ni.

No. of analysis.	Sample.	Weight of nickel bromide in vacuum.	Weight of nickel in vacuum.	Weight of sodium bromide to subtract.*	Weight of nickel bromide corrected.	Weight of nickel corrected.	Atomic weight of nickel.
1.	III.	2·83610	0·76366	0·00285	2·83325	0·76081	58·705
2.	III.	3·21908	0·86641	0·00283	3·21625	0·86358	58·696
3.	III.	2·31578	0·62431	0·00337	2·31241	0·62094	58·703
4.	III.	2·88330	0·77707	0·00377	2·87953	0·77330	58·710
5.	II.	2·29843	0·61872	0·00193	2·29650	0·61679	58·719
6.	II.	2·99118	0·80497	0·00225	2·98893	0·80272	58·714
7.	III.	5·52058	1·48823	0·00767	5·51291	1·48056	58·716
8.	III.*a*	2·25280	0·60726	0·00311	2·24969	0·60415	58·710
						Average..	58·709

* The weights of argentic bromide from which the sodic bromide was calculated were respectively 0·00520, 0·00516, 0·00615, 0·00687, and 0·00352 grm. in Analyses 1, 2, 3, 4, and 5. For Analyses 6, 7, and 8, the figures are given above.

In this series of results, the lowest is 58·696, while the highest is 58·719, a variation ±0·012 from the mean. Adding all the determinations together, 24·31725 grms. of nickelous bromide yielded 6·52286 grms. of pure washed nickel and 0·02778 grm. of sodic bromide, calculated from 0·0507 grm. of argentic bromide. These two weights, taken in connection with the amount of bromine found a year ago, furnish a complete analysis of the best nickelous bromide which we were able to prepare. It must be remembered that 15·51556 grms. of the halide contained, according to two different methods, 11·34985 and 11·34979 grms. of bromine.

It has been already pointed out that this impurity of $\frac{1}{3}$ per cent of sodium would make no difference in last year's results if the "equivalent" of sodium equalled that of nickel. Since, however, it is somewhat less, slightly too much argentic bromide was obtained last year, and the atomic weight of nickel appeared lower than it really is. Assuming the amount of impurity to have been the same in last year's preparation as in this, 0·015 should be added to the atomic weight, in order to correct this error. The results of the four series, which represent the sum and substance of the present research, are then as follows:—Ratios (*e*) and (*f*) were obtained by cross-reckoning from the earlier ratios. The reason for thus re-stating the results is because this re-statement uses the weight of the nickelous bromide only as a constant, and not as a basis of calculation.

Complete Analysis of Nickelous Bromide.

	Per cent.
Nickel	= 26·824
Total bromine = 73·151 % = { Bromine combined with nickel }	= 73·062
Total impurity = 0·114 % = { Bromine actually found in impurity }	= 0·089
Total impurity = 0·114 % = { Sodium	= 0·025
Total	= 100·000

(NOTE.—As has been detailed, some of the earlier preparations contained traces of sulphuric acid in addition. Since this is not taken into account in the average, the sum given is slightly too small, and is perhaps deceptive in its accurate showing. The flaw was eliminated as soon as it was discovered, therefore we had no means of finding the exact amount of the sulphuric acid, but in any case it was so small as to produce only a negligible effect on the result. From some experiments of Mr. Baxter's, it is safe to assume that this error could not have exceeded 0·005 per cent in the worst cases, and in the average it must be still much less).

		Atomic weight of nickel if O = 16·000.
(*a*) Preliminary:	2AgBr : $NiBr_2$ ..	[58·695]
(*b*)	2AgBr : $NiBr_2$ ..	58·703
(*c*)	2Ag : $NiBr_2$ ..	58·704
(*d*)	($NiBr_2$—Ni) : Ni	58·709
[(*e*)]	2AgBr : Ni	58·706
[(*f*)]	2Ag : Ni	58·707
		59·706

If any assurance is needed that this average indicates very nearly the true atomic weight of nickel, the assurance may be found in the review of older work which follows. This review has been postponed until the close of the paper, in order that the methods might be judged in the light of our own experience with the subject.

(To be continued).

Royal Institution.—A General Monthly Meeting of the Members of the Royal Institution was held on the 10th inst., His Grace the Duke of Northumberland presiding, on this the first General Monthly Meeting since his election as President. His Grace announced that the Hodgkins Medal, which is the first gold medal for scientific work ever given by the Smithsonian Institution, has been awarded to Professor Dewar, of the Royal Institution of Great Britain, in recognition of his discoveries in the liquefaction of air; and in so doing he congratulated Professor Dewar on this honour conferred on him, and also on the Royal Institution, which he regarded as specially gratifying as a sympathetic recognition of scientific work and discovery in this country, coming from the Great Nation of our own blood on the other side of the Atlantic. The following were elected Members:—Mrs. Aston, T. O. Belshaw, W. Hall, and Mrs. McClean. The special thanks of the Members were returned to Sir Benjamin Baker, K.C.M.G., for his donation of £50, and to Nobel's Explosives Company for a donation of £105, to the fund for the Promotion of Experimental Research at Low Temperatures.

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THE NATURE OF VALENCE.

By F. P. VENABLE.*

THE term "valence" is variously defined as the "combining capacity," "capacity of saturation," "quantitative combining power," or "chemical value of the atom." It is well known that the introduction of this idea into chemistry was due to the development of the type theory, a system which had at first a purely empirical basis. Sixty years ago there was still some hesitation as to the acceptance of the atomic theory or the need for such a theory. Much use was made of the term equivalent, which had been Wollaston's expedient for avoiding the difficulties arising from the full adoption of the theory of atoms.

Wollaston had been himself very far from consistent in the use of the term. The numbers called by him "equivalent weights" were not unfrequently atomic and molecular weights, and fully as hypothetical as the so-called atomic weights of Dalton. In the later use of the term it signified solely the numbers obtained by analysis without the introduction of any theoretical considerations. Thus, on analysing ammonia, the ratio N : H :: 4·6 : 1 is gotten, and therefore the equivalent of nitrogen is 4·6. Strange to say the equivalent given by Wollaston corresponds with the present atomic weight, whereas the atomic weight given by Dalton corresponds with what would be the equivalent.

It is manifest that the idea of equivalents needed something more than the simple theory of atoms to make it clear and tenable. It embodied two distinct conceptions, and if we hold to an atomic theory we must introduce a further explanatory theory of the saturation capacity of these atoms. This is the theory of valence or quantivalence or atomicity, and without it the equivalents are purely empirical, and it is most difficult, if not impossible, to clear up the confusion connected with their use.

Returning now to the derivation of this idea of valence from the type theory, according to Wurtz ("Histoire des Doctrines Chimiques," p. 69) the conception of valence was introduced into the science in three steps. First there was the discovery of polyatomic compounds. This term was first used by Berzelius in 1827 (*Jsb. d. Chem.*, vii., 89), he applying it to such elements as chlorine or fluorine where he thought several atoms of these elements united with a single atom of another element. The term was later applied by Graham, Williamson, and others to compounds.

The second step was the reference of this polyatomicity to what was called the state of saturation of the radicals contained in these compounds. This was largely through the work of Williamson and Gerhardt.

Thirdly, this conception of saturation was extended to the elements themselves. This was chiefly due to the work of Frankland upon the organo-metallic compounds. And so valence has come to refer to the number of atoms with which a single atom of any element will combine.

This conception has then been one of slow growth, gradually incorporating itself into the science as the necessity arose of devising a suitable explanation for accumulated observations. It was a logical outcome of, and was evolved from, knowledge acquired step by step. It was no mere speculation or hypothesis, such as that of Prout, evolved by the brilliant fancy or imagination of one man, and suddenly appearing with scarcely a claim to foundation upon observed fact.

This conception enters into the chemical theory of to-day almost as fundamentally as the atomic theory itself. Its application is of every-day occurrence and of the most varied character, and yet chemists admit that the nature of valence is one of their chief puzzles, and they have advanced but little towards its solution during the past half-century. It is quite possible that the ideas to be advanced in the further discussion of this subject in this paper will meet with antagonism. Certainly they should be fully and freely discussed if they are worthy of it. I believe that they form a step toward the clearing up of the mystery of valence.

It is necessary, however, first to trace somewhat further the development of the original conception. One of its earliest and most important applications was to the study of the constitution of the compounds of carbon. Here Kekulé assumed for carbon a constant valence of four, and this idea is still dominant in the theories relating to the constitution of these bodies. It was quite natural, then, that the first belief should have been in a constant valence. It was speedily found, however, that in certain cases, as in the compounds of nitrogen and phosphorus, this belief was scarcely tenable. There were efforts at making it hold good, as, for instance, a distinction was drawn between atomic and molecular compounds, but all of these suggestions have been proved unsatisfactory.

We unquestionably have to account for the existence of a compound with three atoms and another with five atoms in the cases of nitrogen and phosphorus, and there are many similar anomalies. Here the valence seems to vary toward one and the same element. Cases might be multiplied to show also that it varies often towards different elements. Thus it frequently happens that the valence of an element towards hydrogen seems to be quite different from that exhibited toward oxygen. For a long time there was much straining to consider the valence of an element always the same; but this effort is, in large measure, abandoned now as unavailing, and chemists admit that valence is not constant, but variable, and may even vary towards one and the same element.

The doctrine of valence has had much added to it about bonds, affinities, and linkage, the necessity for which one may well question. Certainly the misuse of the word affinity here, seeing its other and greater use, should be earnestly discountenanced. I am inclined to think that the other terms bring in false and misleading ideas which should be carefully guarded against. At any rate all hypothetical talk about strong bonds, and weak bonds, double bonds and triple, is to be avoided.

If, then, valence varies, can it be an inherent property of the unchanging atoms? Experiments have shown that it varies with the nature of the combining element, that it varies with the temperature, and with other conditions. It is not dependent upon the atomic weight in the same sense as other properties are dependent upon it. Thus in the same group the valence remains the same whether the atoms weigh nine times as much as hydrogen or two hundred times as much.

We seem shut up to the conclusion that valence is not one of the primitive inherent properties of the atom, but is relative. It is rather to be regarded as the resultant of the mutual influence of the atoms of the combining elements. The clear grasping of the idea is an important step forward. Unfortunately the distinction is not always made nor consistently adhered to.

It may not be amiss to cite here the utterances of Lothar Meyer in regard to the question of a constant or variable valence ("Modern Theories of Chemistry," Eng. Trans., p. 303):—

"Since the aim of all scientific investigation is to exhibit the most variable phenomena as dependent upon certain active invariable factors taking part in them, and in such a manner that each phenomenon appears to be the necessary result of the properties and reciprocal action of these factors, then it is clear that chemical investigation would be considerably advanced were it possible to prove that the composition of chemical compounds is essentially determined by the valency of the atoms and the external conditions under which these atoms react upon one another. The first necessary step in this direction has been made

* Address (as Chairman) delivered before the North Carolina Section of the American Chemical Society. From the *Journal of the American Chemical Society*, xxi., No. 2.

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in the attempt to explain the regularities observed in the composition of chemical compounds, by the assumption of a constant power of saturation or an invariable valency of the atom. The opposite and equally hypothetical assumption that the valency is variable leads to no advancement.

"The first step towards progress in this matter would be made if some hypothesis as to the cause of this variability were proposed. This difference between the two attitudes has seldom been properly realised. While some chemists, accepting the constant valency of atoms, have attempted to deduce the varying atomic linking from one distinct point of view, others have considered it sufficient to have assigned to the atom of a particular element in one compound one valency, and in another compound a different valency, according as this or that value appeared the most suitable, and thus to have given a so-called explanation of the composition of the compounds in question. In this way the fact has been overlooked that an arbitrary interpretation, carried out by means of chosen hypotheses, cannot be regarded as an attempt at a scientific explanation, but is nothing more than an expression of our ignorance of the causal connection of the phenomena. An explanation would require that the different valencies assigned to one and the same element, in different compounds, should be traced to a distinct cause. If, for instance, it is stated that carbon in carbon dioxide possesses double the valency which it possesses in carbon monoxide, such a statement is no explanation of the fact that an atom of carbon in the former compound is combined with twice as much oxygen as in the latter; for such a statement is merely a paraphrase which hides its incompetency by assuming the form of an explanation. Although this may be perceived without further remark, still it has frequently occurred during the past few years that similar paraphrases have not only been proposed, but also accepted as real explanations of such phenomena. Just as it was formerly supposed that the assumption of a vital force dispensed with a more complete investigation of the phenomena of animal life, so many chemists have of late thought that they possessed in 'variable valency' a means of explaining the varying stoichiometric relationships which would satisfy all claims. Such deceptions can only retard the advance of the science, since they prevent an earnest and thorough investigation of the question, whether each atom is endowed with a property determining and limiting the number of atoms with which it can combine, dependent upon the intrinsic nature of the atom, and like it invariable; or whether this ability is variable, and with it the nature of the atom itself."

It is not strange that this line of reasoning should lead Lothar Meyer to doubt the unvarying nature of the atom itself, and thus losing his grasp upon one invariable to make sure of another. He says "It is by no means impossible that the magnitudes which we now style atoms may be variable in their nature."

It will be an unfortunate day for chemists when the belief in the unchanging atom is given up. Chaos will indeed enter into all of our theories when this, the foundation rock, is left at the mercy of every shifting tide of opinion, and can be shaken by all manner of unfounded hypotheses.

The case cannot be so hopeless as to necessitate calling to our aid so dangerous a doctrine. Before turning to such an expedient let us first make all possible use of our atomic theory as it stands. The extension of this theory teaches that the atoms are endowed with motion, and this motion probably varies in velocity and phases with the different elements. So, too, when the atoms unite the resulting molecule has a certain motion peculiar to it, while the atoms composing it have an intra-molecular motion in which their original motions are probably modified by their influence upon one another. It is quite manifest, then, that a molecule, in order to exist, must maintain a certain equilibrium and harmony between these various motions, and that there can be all degrees of equilibrium from the very stable to that which may be upset by the least disturbing influence from without.

It seems to me that herein we have a full and satisfactory means of explaining the various problems connected with the conception of valence. The question as to whether the atoms of two elements will unite is decided by affinity, which is in some way connected with the electrical condition of those atoms. There is no apparent connection between this and valence. The number of atoms which enter into combination forming one molecule is purely a matter of equilibrium, and is dependent upon the motion of those atoms. Thus a phosphorus atom unites with chlorine atoms because of a certain affinity between them. The number of chlorine atoms with which it will unite depends upon the possibility of harmonising the respective motions. As the temperature may affect these motions, and also impart a more rapid molecular motion, it is evident that the harmony, or equilibrium, will depend upon the temperature, and that a temperature may be reached at which no harmony is possible, and hence no compound can be formed. The phosphorus atom mentioned can, as we know, form a stable molecule with five atoms of chlorine. On increasing the temperature this becomes unstable, and only three atoms can be retained. Neither with four atoms nor with two is there harmony of motion. A sufficiently high temperature may prevent any harmony of motion whatever being attained, and hence union may become impossible.

As to other influences than those of temperature, we can see that the equilibrium between the atom of phosphorus and the five atoms of chlorine may be upset by such a molecule coming within the influence, electrical or vibratory, of a molecule of water. The atoms must re-arrange themselves for a new state of equilibrium, and so an atom of oxygen takes the place of two atoms of chlorine, giving again a condition of harmony. In other cases the motion of the molecule of water may be of such a character as to directly harmonise with that of the original molecule, and so to enter into equilibrium with it, a definite number of such molecules of water affording a condition of maximum stability. This we call water of crystallisation. Such molecules would be more or less easily separated by an increase of temperature, and, where several molecules of water were attached, the highest temperature would be necessary for freeing the original molecule from the last water molecule.

A carbon atom finds its most perfect state of equilibrium where four atoms of hydrogen or their equivalents move in harmony with it. But there is a second state of equilibrium where only half that number of atoms are moving with it. This state does not seem to be a possibility where these are hydrogen atoms, but is readily possible where the equivalent number of oxygen atoms is concerned. Such a molecule, however, is always in a condition to take up additional atoms until its highest equilibrium is reached, and in doing this it proceeds by the regular steps needed for bringing about a harmony of motion. A molecule in a lower state of equilibrium we have become accustomed to call unsaturated, calling that one saturated which is in its highest state of equilibrium. The further application of this hypothesis is easily made, and need not be dwelt upon here. It will be helpful in many ways,

This theory of valence makes it clear why it should vary toward the same element under different conditions. It is also clear that it might vary towards different elements, as these are very possibly possessed of different motions. It is further evident that it is in accord with the conclusion that valence is not an inherent property of the indivdiual atom, but is the resultant of the influence upon each other of the combining atoms.

Only one point remains to be considered: Why do the elements of the same group have practically the same valence? The nearest answer to this, and it seems satisfactory, is that they are all possessed of the same

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phase or kind of motion. In other words, the natural division into periods gives us seven or eight more or less different phases. These are, in large measure, independent of the atomic weight. And so the elements in any given group have the same tendency towards similar states of equilibrium in forming compounds with any other element, as hydrogen or oxygen. Some elements—as copper, mercury, tin, &c.—are peculiar in that they may change their phase of motion under certain influences, acting then as if they belonged to different groups, and entering into totally different states of equilibrium in forming their compounds.

Lastly, it is possible for a combination of atoms of different elements, as NH_4 or CN, to have such molecular and intra-molecular motion that, although not in a state of equilibrium themselves, they are capable of entering into such states just as the single atoms of elements do, having apparently similar valence.

I might develop this theory much further, but it is unnecessary now. Enough has been said to show that such an application of the atomic theory is legitimate and is most highly important as a step towards the clearing up of the problems springing from the conception of valence and from the Periodic System.

NOTE.—Since certain points in this paper require treatment at greater length than was practicable in an Address, it will be followed by a second paper elaborating such portions.

CORRESPONDENCE.

THE 32 EQUIVALENT AND ITS RELATION TO THE PERCENTAGE OF AVAILABLE SODA IN CAUSTIC SODA.

To the Editor of the Chemical News.

SIR,—As I am the compiler of the tables printed in Dr. Lunge's "Treatise on Alkali Manufacture" quoted by Mr. H. A. Hooper in his letter to the CHEMICAL NEWS (vol. lxxix., p. 155), I may be allowed to point out that Mr. Hooper misunderstands the meaning of the soda figures given by the English alkalimetrical test. He is under the mistaken impression that the English test gives the *percentage* of soda in caustic soda calculated upon the 32 equivalent for soda; and that, consequently, if pure caustic soda be tested by English test-acid it will indicate 78·05 per cent of soda. This is not the case. If pure sodium hydrate, containing actually 77·5 per cent of soda be tested with English test-acid, it will indicate 78·52 English (or, as Dr. Lunge calls them, "Newcastle") degrees of soda—a number which is higher than the true percentage of soda by 1·02, as indicated by the tables.

English test-acid was used originally only for testing the percentage of soda in soda-ash and alkali; caustic soda not being at that time an article of commerce. The strength of the test acid was based upon the old and erroneous assumption that the equivalent of soda was 32, and that, therefore, pure carbonate of soda contained 59·26 per cent of soda. As a matter of fact, pure carbonate of soda really only contains 58·49 per cent of soda—the true equivalent of soda being 31 and not 32. English test-acid is therefore weaker than test-acid made on the correct equivalent of soda, and it indicates in titration an amount of soda greater than the true amount in the ratio of 59·26 : 58 49. When, later, caustic soda was manufactured, the same test-acid was—and still is—used for testing it as had been used for testing alkali, and the figures so obtained were commonly (but erroneously) called "percentages" instead of "English alkalimetrical degrees." It is true that when testing carbonate of soda English test-acid indicates the percentage of soda based on the 32 equivalent, but this is only true in the case of carbonate of soda. When any other compound of soda neutralisable by acid is tested by English test-acid, the English degrees of soda indicated are not percentages. It will be seen from the above that, in order to calculate the percentage of soda indicated by 31 equivalent test-acid into the corresponding English alkalimetrical degrees, it must be increased in the ratio of 58·49 to 59·26.

I quite endorse Mr. Hooper's opinion that it is highly desirable, for the sake of scientific accuracy, that the use of the 32 equivalent should be abolished.—I am, &c.,

JOHN PATTINSON.

75, The Side, Newcastle-on-Tyne,
April 4th, 1899.

THE 32 EQUIVALENT AND ITS RELATION TO THE PERCENTAGE OF AVAILABLE SODA IN CAUSTIC SODA.

To the Editor of the Chemical News.

SIR,—Mr. H. A. Hooper, of Chicago, in the CHEMICAL NEWS of March 30th (vol. lxxix., p. 155) expresses his astonishment that a very serious error in the reduction of the true percentage of Na_2O to that calculated on the false 32 equivalent for Na_2O "should have been made and remained undetected by Prof. Lunge."

Mr. Hooper's astonishment ought to extend infinitely further; for precisely the same error must have been "made and remained undetected" by Mr. John Pattinson, who originally calculated (as stated in my book) the table quoted by Mr. Hooper, and by the thousands of chemists who have since that time used it.

But every reason for astonishment disappears to him who reads the explanation as given on page 106 of my book, just before the table itself. If Mr. Hooper had taken that trouble, he would have found what Mr. Pattinson, as well as myself and the rest of the world, understand by "Newcastle degrees" or "Tyne test"—something very different from Mr. Hooper's calculation. Those conventional degrees were originally intended for carbonate of soda, and have been later on applied (partly by extrapolation) to caustic soda. In the above-quoted place, Mr. Hooper will find that there are several other ways of using, or rather misusing, the 32 equivalent, and his own way of calculation adds one to the list.

In one respect I entirely agree with Mr. Hooper, viz., that the 32 equivalent should entirely disappear. On page 107 of my book he will find that I have done my level best in that direction for twenty years past; unfortunately not with sufficient success, since the "vested interests" of Liverpool are against it.—I am, &c.,

G. LUNGE.

Zürich, April 6, 1899.

ESTIMATION OF POTASH.

To the Editor of the Chemical News.

SIR,—With reference to my note on "The Estimation of Potash" (CHEMICAL NEWS, vol. lxxix., p. 135) and the remarks thereon (p. 154), I would say that the two processes are totally different; the essential part of mine being the addition of barium carbonate (already existing as such) to a slightly alkaline solution.

If ammonia is added to produce a *slight* alkalinity, and a *considerable excess* of barium carbonate used, the precipitation of sulphates is perfect. Probably this would not be the case if the ammonia were in considerable excess and only a small amount of the barium salt used; this, however, is guarded against if the directions are followed.—I am, &c.,

E. WIGHTMAN BELL.

High Bridge, Spalding, April 6, 1899.

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CHEMICAL NOTICES FROM FOREIGN SOURCES.

Note.—All degrees of temperature are Centigrade unless otherwise expressed.

Comptes Rendus Hebdomadaires des Séances, de l'Académie des Sciences. Vol. cxxviii., No. 12, March 20, 1899.

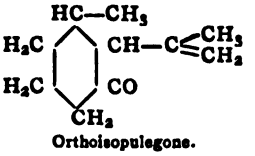
Action of Hydrogen Sulphide and of the Alkaline Sulphides on Double Cyanides; Cyanosulphides.—M. Berthelot.—The author states that, in presence of alkali, solutions of double cyanides are not precipitated by hydrogen or sodium sulphides. Freshly precipitated silver sulphide was washed with a solution of potassium cyanide, and filtered after a few minutes. The filtrate contained a considerable quantity of silver as double cyanide, together with potassium sulphide and potassium cyanide in excess. The addition of hydrogen sulphide gave no sensible precipitate, but on adding acetic acid, an abundant black precipitate of silver sulphide was obtained. The action of the hydrogen sulphide is dependent on the extent to which the potassium cyanide is present in excess; complete precipitation being effected without the addition of acetic acid if the cyanide is only in small excess. Hence, the stability of the argento-hydrocyanic acid present in the system increased with the excess of alkaline cyanide. Mercuric sulphide was not dissolved to an appreciable amount by potassium cyanide, but readily dissolved in sodium sulphide and in the absence of cyanides. From this solution it was re-precipitated on acidifying. The stability of the soluble double sulphide increases with the excess of the alkaline sulphide. On treating a solution of the double cyanide of zinc and potassium with hydrogen sulphide, the results obtained accorded with those of the double cyanide of silver and potassium under similar conditions.

An Isomer of Menthoxylic Acid.—Georges Leser.—Not suitable for abstraction.

Silico-tungstic Acid as Reagent for Alkaloids.—M. Duclaux.—The author has obtained well-defined stable salts of the alkaloids with silico-tungstic acid, which makes the latter valuable as a reagent. This acid, $12WO_3.SiO_2.2H_2O$, is the most sensitive of all the reagents, and the alkaloids are very easily extracted from the insoluble compounds it forms with them. The general type of these compounds is $12WO_3.SiO_2.2H_2O.4Alk. + nH_2O$. They are obtained as white or pale coloured precipitates from cold solutions of the salts of the alkaloids. They are almost insoluble in both hot and cold water, are unattacked by acids, and after calcination leave a residue of constant composition, consisting of silicic and tungstic acids. Oxidising agents decompose the silico-tungstates of the alkaloids. The alkaloids are re-generated by addition of dilute alkali, even of ammonia, the silicon and tungsten passing into solution.

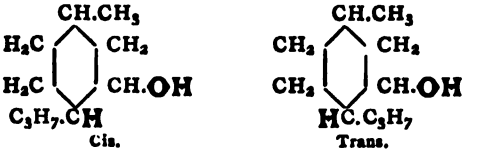
Liebig's Annalen der Chemie, April 18, 1898.

Research on the Terpenes and Essential Oils.—O. Wallach.—Pulegenic acid is an isomer of campholenic and phenolenic acids, and is produced by the action of alkalis on the dibromide of pulegone, $C_{10}H_{16}OBr_2$. It must be purified by distillation *in vacuo* immediately after its preparation. Hydrochloropulegenate of methyl, $C_{10}H_{16}Cl_2O_2$, treated on the water-bath with sodium and methanol, gives pulegenate of methyl, $C_{10}H_{15}O_2CH_3$, which distils at 89—90° under 10 m.m.; but, at the same time, there is partial saponification and formation of a lactone, $C_{10}H_{16}O_2$, isomerous with pulegenic acid. When we add a solution of BrOK to a concentrated solution of pulegenic acid in potash, an oil separates which is a bromised lactone. Although pulegone can be split up into methylhexanone and acetone, the body formed by the condensation of these two is not identical, but isomeric. The author assigns to this isomer the constitution—



Orthoisopulegone.

On the Isomerics Cis- and Trans- in the Menthol Series.—O. Wallach and D. E. Werner.—Wallach has shown that, in the reduction of left-handed menthenoxime, a left-handed menthylamine is formed, while menthone furnishes—besides the left-handed amine—a right-handed menthylamine by the action of formate of ammonium. The difference between the right-handed or *cis*-menthol and the left-handed or *trans*-menthol is shown by the following formulæ—



Cis. Trans.

On a New Camphor: Pinocamphone.—O. Wallach and J. A. Smythe.—Pinylamine, $C_{10}H_{15}NH_2$, obtained by the reduction of nitrosopinene, gives, with nitric acid, an alcohol, $C_{10}H_{15}OH$; and this, by oxidation, a ketone, $C_{10}H_{14}O$. The alcohol is pinocarveol, and the ketone pinocarvone. This latter easily gives a semicarbazone, $C_{10}H_{14}N.NH.CONH_2$, fusible at 204°, but not well crystallised. Pinocamphone is obtained by the reduction of nitrosopinene; it is an isomeric ketone of camphor. Its odour is somewhat like that of turpentine, and when warmed recalls that of menthol; it boils at 211—213° at the ordinary pressure; its density is 0·959; $n_D = 1·47273$.

On Phenone.—O. Wallach.—The author finds that phenone-carbonic acid, which he has attempted to purify, is in reality a mixture of two isomers. After having added water to the product of the reaction of CO_2 on phenone in the presence of sodium and absolute ether, the aqueous layer is exhausted with ether to remove the phenylic alcohol; the phenone-carbonic acid is then at once set at liberty by a quantity of acetic acid necessary to saturate the sodium used; the free acid is removed by means of ether, and the ethereal solution distilled *in vacuo*. There first passes over, between 80° and 150°, a liquid product; then, from 150° to 180°, a product which solidifies; after that, other products which will be examined later on. Pure α-phenone-carbonic acid, $C_{10}H_{16}(OH)CO_2H$, crystallises in acetic acid in transparent pointed prisms fusible at 141° to 142°; it distils without decomposition at 175° (11 m.m.). β-Phenone-carbonic acid crystallised in acetic acid in confused crystals melting at 76—77°; it is dextrogyre, but less so than the α-acid; it is also much less stable, and is decomposed by heat, losing either CO_2 or H_2O, giving either phenylic acid or anhydrophenone-carbonic acid. The isomerism between the α and β acids appears to be physical; α being a *trans*-compound, and β a *cis*. The products of oxidation with MnO_4K acid are the same—phenone is formed.

On Cinchotine.—Zd. H. Skraup.—A controversial paper, not suitable for abstraction.

Spontaneous Racemisation. — P. Walden. — The author shows that the rotatory power of the derived halogens is extremely unstable when the halogen atom is united directly to the asymmetric carbon. Racemisation is not always accompanied with decomposition.—*Berichte der Deutschen Chemischen Gesellschaft.*

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MEETINGS FOR THE WEEK.

MONDAY, 17th.—Society of Arts, 8 (Cantor Lectures). "Leather Manufacture," Prof H. R. Procter, F.I.C.

TUESDAY, 18th.—Royal Institution, 3. "Zebras and Zebra Hybrids," by Prof. J. Cossar Ewart, M.D., F.R.S.

—— Society of Arts, 8. "Inlaying," by Stephen Webb.

WEDNESDAY, 19th.—Society of Arts, 8. "London's Water Supply," by Walter Hunter, M.Inst.C.E.

—— Microscopical, 8. "The Bioplasm of Man and the Higher Animals, and its Influence in Tissue Formation, Action, and Metabolism—a Microscopical Study," by Prof. Lionel S. Beale, F.R.S.

—— Institution of Mining and Metallurgy, 8. Presidential Address. "Notes on the Alleged Shortage in Cyanide Bullion," by C. W Merrill, Assoc.Inst.M.M. "Chemical Reactions involved in the Amalgamation of Silver Ores," Henry F. Collins, M.Inst.M.M.

THURSDAY, 20th.—Royal Institution, 3. "The Atmosphere," by Prof. Dewar, M.A., LL.D., F.R.S.

—— Chemical, 8. "Some Dipyridyl Derivatives from Citrazinic Acid," by W. J. Sell, M.A., and H. Jackson, B.A., B.Sc. "Interaction of Mercurous and Mercuric Nitrites with the Nitrites of Silver and Sodium," by P. C. Ray, D.Sc. "Synthesis and Preparation of Terebic and Terpenylic Acids," by W. Trevor Lawrence. "Allotropic Modifications of Phosphorus," by D. L. Chapman. "β-Isopropyl-glutaric Acid," by F. H. Howles and J. F. Thorpe. "Ethyl-ammonium Sulphite," by Edward Divers and Masataka Ogawa. "Ethyl-ammonium Selenite and Non-existence of Amido-selenites (Selenosamates)," by Edward Divers and Seihachi Hada.

FRIDAY, 21st.—Royal Institution, 9. "Structure of the Brain in relation to its Functions," by Frederick Walker Mott, M.D., F.R.S.

—— Physical, 5. "Effect of a Solid Conducting Sphere in a Variable Magnetic Field on the Magnetic Induction at a Point Outside," by C. S. Whitehead, M.A. "Demonstration of Richards's Method of Standardising Thermometers," by R. A. Lehfeldt, D.Sc.

SATURDAY, 22nd.—Royal Institution, 3. "Machiavelli," by Louis Dyer, M.A.

NOTES AND QUERIES.

*** Our Notes and Queries column was opened for the purpose of giving and obtaining information likely to be of use to our readers generally. We cannot undertake to let this column be the means of transmitting merely private information, or such trade notices as should legitimately come in the advertisement columns.

Wolfram.—Can any correspondent inform me what are the present uses of this mineral and what price wolfram ore commands? —A. J. W.

TO CORRESPONDENTS.

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THE CHEMICAL NEWS.

Vol. LXXIX., No. 2056.

ON CRUCIBLE STEEL.

By SERGIUS KERN, M.E., St. Petersburg.

More remarkable results than my own have been obtained by M. Reyher, at the Baltic Works, in casting various hollow thin steel castings for the different and complicated fittings of marine water-tube boilers. Crucible nickel steel is used; the furnaces working with naphtha give a highly-heated soft steel, having good fluidity, which is so essential for the success of castings with a thin body.

The naval authorities prescribe the following tests:—Absolute resistance 28 to 35 tons per square inch, with an elongation not less than 14 per cent, in a length of 2 inches; bending test, 90° at 28 tons and 60° at 35 tons. Hollow castings for water-tube boilers are tested also under water-pressure; some of them must stand 450 lbs., other more responsible fittings 600 lbs. per square inch.

The Baltic Works steel castings not only fulfil such requirements, but give, with an absolute resistance of 32 to 34 tons, an elongation near and sometimes over 20 per cent. The bending tests are splendid, and cannot be compared with the results given by ordinary carbon mild steel. Nickel steel, containing about 2 per cent of nickel, is the best material for thin hollow castings.

In conclusion, I desire to give a preliminary notice that, for some time past, I have been experimenting to purify pig-irons from noxious elements, by means of hydrogen and some other gases. In preparing high-class crucible tool steel, wrought iron free from sulphur and phosphorus is necessary, but the price of such iron is often an obstacle. If we can get a quick method for removing sulphur and phosphorus from various pig-irons, we may say that such a problem will be beneficial to steel producers.

New Admiralty, April 6, 1899.

NEW METHOD FOR THE PRODUCTION OF HIGH TEMPERATURES, AND FOR THE PREPARATION OF DIFFICULTLY FUSIBLE METALS, FREE FROM CARBON.

By M. GOLDSCHMIDT.

The author first passes in review the different researches which have been made on the use of aluminium for the production of high temperatures, and then describes the method he has adopted.

We know that the combination of aluminium and oxygen gives rise to an extremely violent reaction, of which the temperature is estimated to be about 3000° C. To utilise this temperature practically, the principal difficulty seems to be in regulating the reaction by means of which the work is performed.

The first point to note is that there is no need to heat the whole of the reacting mass up to the temperature of ignition; it suffices to cause combustion at one single point. But in this there is still a practical difficulty to overcome. In the preparation of metallic chromium, starting with a mixture of oxide of chromium and powdered aluminium, this difficulty can be easily overcome by placing at a convenient point a small quantity of a mixture of aluminium with a more easily reducible oxide, or, better still, with a peroxide. Oxide of lead, oxide of copper, permanganate of potash, and other substances, may be used for this purpose.

The great advantage of this method is that it enables us to prepare the pure metals, free from aluminium; the only precaution to take is to employ a slight excess of the oxide to be reduced.

The process is capable of two principal applications. In the first place, the heat given off by the combustion of a mixture of aluminium and a suitable oxide can be used simply as a source of heat (for soldering, welding, &c.). In the second place, the reducing power of aluminium, at a high temperature, can be utilised in the preparation of pure metals and of alloys. In both cases the method of working is practically the same.

If we only desire to produce a moderate heat the reacting mass is diluted by the addition of some inert substance, which at the same time prevents the fusion of the mixture. A very good mixture of this nature is composed of aluminium and some cheap oxide, such as oxide of iron, sand, &c., to which may be added lime, magnesia, &c. If, on the contrary, we wish to produce a reduction to the metallic state, we must be careful not to use too great a proportion of oxide, in such a manner that the heat given off by the reaction will melt not only the reduced metal, but also the slag. This latter will then protect the metal against any oxidising action of the air.

I now give a few experiments which form so many interesting applications of this process.

A rivet, weighing 3 kilogrms., such as are employed in bridge-making, is imbedded in a mixture of oxide of iron, sand, and aluminium powder. The whole is plunged in sand contained in a wooden box. On the top of the aluminium mixture, which must just emerge from the sand in the box, we place a small lump of a mixture of aluminium powder and an easily reduced oxide, in which is fixed the end of a short piece of magnesium ribbon. The reaction is started by lighting the free end of the magnesium, and we then immediately place more sand on the top of the mixture, so that as little heat as possible may be lost. If, at the end of a few moments, we empty out the contents of the box, the rivet will be found to be quite red-hot and ready to be forged.

Working in an analogous manner, we can weld together steel tubes of 2·5 c.m. diameter, and the expense will not be more than twopence. We can even fuse together two bars of soft steel.

By diminishing the quantity of inert material used in the preceding experiments, iron can be easily melted.

To reduce oxide of chromium it must be mixed with a suitable quantity of aluminium, and placed in a crucible brasked with magnesia. The reaction is started in the manner described above, and we go on adding the mixture until the crucible is full. After cooling, we break the crucible and take out the ingot of metallic chromium. The author has presented to the German Electrochemical Society a block of metallic chromium weighing 25 kilogrammes, prepared by this method.

By arranging two orifices in the crucible, one for the introduction of the mixture and the other for the escape of the metal, we can make the operation continuous, as in the electric furnace.

According to the author, the temperature obtained under these conditions is higher than that realised in the electric furnace, and we can reduce a given quantity of a metallic oxide in a much shorter space of time, and, further, the metal obtained is entirely free from carbon and carbides. The slag (alumina) obtained can be used over again for the production of aluminium, or it may be utilised as a polishing material; it has, in fact, great advantages over emery.

Nearly all the metals can be reduced by this method, and the return is almost theoretical. We can also prepare alloys such as those of chromium and manganese, copper and chromium, &c., by the same method.

For the preparation of pure metals it is necessary to

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use only pure aluminium, but for simple heating operations the metal at 50 per cent purity will suffice. Besides the oxides we can also reduce the oxysalts of certain metals.

The author looks upon aluminium as a *heat accumulator*, since its utilisation as a reducing agent allows of the regeneration of a quantity of energy, corresponding to that required for its precipitation.—*Zeits. für Electrochemie*, 1898, iv., 21, p. 494.

THE ESTIMATION OF LEAD IN ITS ORES.

By F. MOLDENHAUER.

There are a number of well-known methods giving perfectly exact results, but they nearly all necessitate the use of a large amount of apparatus, reagents, &c., which prevents them being used universally. I propose describing a method I have devised and which has given me excellent results.

In the case of ores containing less than 30 per cent of lead, we take 2 grms. of the material and reduce it to a fine powder. We then boil with strong hydrochloric acid until the attack is complete and no more bubbles of gas are given off. When we have to do with ores very rich in antimony, it is better to evaporate three or four times, in the presence of strong hydrochloric acid; in this way all the antimony is eliminated. We then add nitric acid, drop by drop, and evaporate to dryness rapidly to destroy the sulphides.

The residue is taken up with the necessary quantity of hydrochloric acid, 80 to 100 c.c. of water are added, the whole brought to a boil and filtered as hot as possible into a flask or a matras. Wash, as hot as possible, with water acidulated with hydrochloric acid, to dissolve all the chloride of lead. The filtrate is heated, ammonia added (but not enough to produce a precipitate), and submitted while warm to the action of sulphuretted hydrogen. The precipitate formed is thrown on a filter and washed, first with water and then with warm sulphide of ammonium; it is compressed between two sheets of filter-paper, and placed in a porcelain crucible of 50 or 60 c.c. capacity, which must be covered with a watch-glass, after having added some concentrated nitric acid. We then evaporate to dryness over a small flame, and calcine in the presence of air; allow to cool, and repeat the same treatment; after this we add concentrated sulphuric acid, bring to boiling for a moment, and after complete cooling add water, boil again, then throw the sulphate of lead formed on a filter. After desiccation, remove the sulphate of lead from the filter and place it in a porcelain crucible, burn the filter separately, and weigh the whole after calcination.—*Chemiker Zeitung*, 1898, p. 256.

THE ESTIMATION OF PHENOLS IN DISINFECTANTS IN THE PRESENCE OF SOAP.

By M. W. SPALTEHOLE.

Several different methods have been proposed for the estimation of phenols in the presence of soap.

A. Blomquis recommends simply submitting the product to distillation at 210°. But, as he himself admitted, this separation is not sufficient to isolate the whole of the phenols. To obviate this inconvenience he suggests a correction, the value of which is, however, very problematical.

M. Fresenius and C. Martin add a mineral acid to the product, distil the liquid in a current of steam, and estimate the phenols in the distillate by Koppeschaar's method.

The author has noticed that the addition of a mineral acid to the product is not necessary in the case of disinfectants which have a neutral reaction, and therefore contain free phenol, as, for example, creoline, lysol, soluble cresol, &c. He estimates the phenols in these products in the following manner:—The material to be analysed is heated, in an iron vessel for preference, to a temperature of 200°, a current of steam is passed through it, and the temperature increased to 220°: this operation is continued until the current of steam no longer carries over any oily drops. If we have to deal with products containing oleic soaps the temperature must not exceed 210°, for at about 220° these soaps are decomposed by steam, and oleine passes over into the distillate. Resin soaps do not decompose even at 220°. The distillate contains either phenols only, as with lysol, or phenols mixed with the hydrocarbons of the tarry series, as with creoline. The phenols thus isolated can be estimated either direcly or in the combined state. The simplest method consists in exhausting the distillate with benzene, and estimating the phenols in the benzenic extract by means of a titrated solution of caustic soda.

The author has himself prepared and analysed a series of products by this method. The results obtained were at the most not lower than 0·5 to 1 per cent of the actual proportion of phenols present in the soap. These results may be considered as sufficiently exact for determining the quality of commercial disinfectants.

The proportion of lysol in phenols varied in the different products examined, from 40 to 60 per cent.

As for commercial creolines, the author has found that the proportion of phenols present varies from 0 to 20 per cent. One creoline contained as much as 28 per cent of phenols, but it did not give a good lather with water. In creolines giving a good, persistent lather, the proportion of phenols present does not exceed 18 per cent. If we take the proportion of phenols present as a basis for estimating the disinfecting power of the products, it must be remembered that lysol is much more powerful than creoline. However, in this latter it is not only the phenols that act as antiseptics; they also contain hydrocarbons of the tarry series, which exercise, according to the researches of Prof. Forster, an appreciable bactericidal action.—*Chemiker Zeitung*, 1898, p. 58.

ON THE METHODS EMPLOYED IN THE ANALYSIS OF COMMERCIAL AMMONIA.

By A. LUNGE and W. HEFTER.

A certain number of papers have been recently published having for their subject the analysis of commercial ammonia.

Lange and Hertz (*Zeitschr. f. Angew. Chem.*, 1897, 224) collected the ammonia in an open receiver, while Bunte and Eitner (*Journ. f. Gasbel und Wasservers.*, 1897, 174), the same as Urban (*Chem. Zeit.*, 1897, p. 720, and *Moniteur Scientifique*, 1898, p. 68) put the reservoir in direct communication with a closed vessel, and filled this latter by pressure. The method utilising a closed vessel would have the advantage of preventing any error resulting from evaporation during the collection of the sample.

We now propose to review these different methods.

We will first briefly describe the Bunte-Eitner method. Into a glass pipette furnished with a stopcock at each end, we pass the ammonia directly from the reservoir and weigh it. We then place the pipette in a vertical position and connect it with three absorption-tubes filled with solid potash, the weights of which have been accurately determined. We then open the upper stopcock of the pipette, so as to allow the gaseous ammonia to slowly traverse the potash-tubes. After the evaporation of the liquefied ammonia we place the pipette, in a horizontal

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position, in a hot-air oven, which must be gradually heated to 70—80°; at the same time we pass a current of dry air, free from carbonic acid, through the apparatus for some time.

If it were true that this method gives accurate results, we ought to find the impurities which accompany the ammonia in the absorption-tubes, such as water, pyridine, naphthalene, ethylic alcohol, acetonitrile, benzol, &c. But in practice this is not the case; all these bodies are volatile at 70—80°; they are carried away with the current of gas, and are only found in minute quantities in the absorption apparatus. It is therefore evident that the method in question does not give anything like exact results.

It is true Urban has improved the Bunte-Eitner process, inasmuch as, leaving the absorption-tubes alone, he weighs the residue from the evaporation, after heating to 30° only. It is a fact that a certain quantity of ammonia remains dissolved in this residue, but the resulting error is so small that it may be neglected.

For the purpose of comparing Urban's method with that of Lange and Hertz we have prepared different mixtures, of which the composition was accurately known. These mixtures were made with pure ammonia (with 0·2 per cent residue), with benzol, alcohol, pyridine, and water, and with residues from various samples of ammonia. The following are the results we obtained:—

Nature of impurity.	Calculated p.c.	Found afterwards. Urban.	Found afterwards. Lange and Hertz.	Per cent. Urban.	Per cent. Lange and Hertz.	Mean.
Benzol	1·5	0·99	1·7	66	113	—
,, ...	1·5	0·75	1·5	50	100	—
,, ...	1·5	1·13	1·5	75	100	—
,, ...	1·5	0·77	1·0	51	67	—
,, ...	1·5	0·76	1·0	51	67	—
Pyridine ..	1·0	0·65	1·2	65	120	—
,, ...	1·0	0·70	1·1	70	110	—
Water	1·1	0·91	1·2	83	109	—
Alcohol	1·0	0·80	1·6	80	160	—
,, ...	1·0	0·79	1·8	79	180	—
Alcohol and acetonitrile .	1·0	0·79	1·5	79	150	—
Alcohol and benzol ..	1·3	0·79	1·4	61	108	—
Benzol and pyridine ..	1·0	0·80	0·9	80	90	—
,, ,,	1·0	0·66	1·1	86	110	—
Residue A ..	1·0	0·54	1·1	54	110	82·0
,, ..	1·7	1·41	1·9	83	112	97·5
Residue B ..	1·1	0·74	1·5	67	136	101·5
,, ..	2·2	1·54	2·8	70	127	98·5
,, ..	2·7	2·04	3·1	76	115	95·5
Residue C ..	1·0	0·80	1·3	80	130	105·0
,, ..	1·7	1·33	2·2	78	130	104·0
Mean of all the samples	—	—	—	72	120	96 0
Mean of the 7 last samples	—	—	—	72	123	98·0

It will be seen that neither of these two methods is rigorously exact; Urban's method gives figures which are too low, while those of Lange and Hertz are too high. As there can be no loss of ammonia in the taking of the sample, it must be admitted that a portion of the impurities has been mechanically carried over by the ammonia gas. The quantity of these entangled impurities varies considerably from one sample to another—it depends on the nature of the body present. Benzol and pyridine are the most easily carried over, while alcohol and water are more difficult; among the mixtures, that composed of equal parts of alcohol and pyridine is the most difficult to be carried over.

These considerations enable us to explain how it is that sometimes the Lange-Hertz method gives perfectly exact results. We have also a word to say about the method used in America and Australia for the examination of commercial ammonia. In these countries it is required that the ammonia, transferred from the reservoir to an open vessel, should have a boiling-point of 33·7° C.; a higher boiling-point denotes a less pure product. But we have observed that this method is very unsatisfactory, and that it does not enable one to distinguish with certainty between a product containing 0·1 per cent of impurity and another containing 1·0 per cent.

Thus all the methods which have up to now been recognised in the analysis of commercial ammonia are sullied with grave errors, and cannot be used when scientifically exact results are required.

But, we may ask, is it really necessary, commercially, to have absolutely correct results? Liquid ammonia is almost exclusively used for the manufacture of ice, and it is evident that its refrigerating action will be the greater the purer it is; but, on the other hand, we do not think that small quantities of impurities can have any very serious action. It is not really indispensable to know whether a given ammonia contains 1 per cent or 1·2 per cent of impurities; we must, however, insist that such impurities should not exceed a maximum limit, which will vary from one case to another, according to the wants of the consumer. Now to determine the permissible amount of these impurities, which of these two methods in question should we advise? One gives too high results and the other too low; but the mean of the two more often approaches the truth, as will be seen in the above table.

The Lange-Hertz method is very easy to perform, and we do not hesitate to recommend it, whatever may be said for Urban's, until we have succeeded in finding a really exact method.—*Die Chemische Industrie*, 1898, p. 2.

A NEW METHOD FOR THE DETERMINATION OF ZINC.

By A. C. LANGMUIR.

Practically two methods only are in general use for the gravimetric determination of zinc. Of these the carbonate method, with its many imperfections, is being displaced by the phosphate method, at least in this country.

With care the latter will yield excellent results. In our practice it is customary to use ammonium phosphate in place of the usual sodium salt (Garrigues, (*Journ. Amer. Chem. Soc.*, xix., 934), and after the precipitation of the phosphate to destroy the slight excess of ammonia remaining after heating on the water-bath, by the cautious addition of dilute acetic acid. Under these conditions the filtrate is free from zinc.

Directly igniting the sulphide and filter, and weighing as oxide or sulphide, has been used, but is open to serious objection if the amount of zinc is at all large.

As far as we are aware no one has proposed the solution of the sulphide in nitric acid, the evaporation of the solution so obtained, and the conversion of the residue to oxide by ignition. As a second precipitation and washing is avoided it is quicker than the carbonate or phosphate methods, and is preferable to the latter in that the impurities almost invariably present in the zinc precipitate may be easily determined and allowed for.

The sample of ore for analysis (½ to 1 grm. according to its zinc content) is dissolved, and the metals precipitated by hydrogen sulphide separated by the usual methods. After expelling hydrogen sulphide the solution is coloured by bromine water, and the iron and any manganese present are separated by ammonia. The precipitate is dissolved in hydrochloric acid, and the precipitation is repeated a second or third time if necessary.

If the ore is one which is known to be free from lime and magnesia, the combined filtrates may be boiled down

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immediately, with the addition of an excess of nitric acid, to destroy chlorides and ammonium salts. After the removal of the chlorine, the solution is transferred to a weighed platinum dish, evaporated to dryness, ignited, and weighed as oxide.

The troublesome filtration and washing of the zinc sulphide should be avoided if possible. In our opinion better results are obtained by the ferrocyanide titration of the solution of the unwashed sulphide than by any gravimetric method involving the filtration and *washing* of this precipitate.*

The zinc is best precipitated as follows:—Acidulate the warm ammoniacal filtrate from the iron with hydrochloric acid, add a few drops of sulphurous acid to neutralise the bromine set free, then three or four drops of methyl orange.† Neutralise with ammonia carefully, and add ammonium sulphide drop by drop, with constant stirring, until a drop of the solution gives a dark colouration with a drop of dilute ferric chloride solution on a porcelain plate, showing a slight excess only of ammonium sulphide. The liquid is now warmed on the water-bath until the sulphide is settled, and is filtered through a double-ribbed filter. Under these conditions a clear filtrate is invariably obtained, but if washing is attempted the filtrate is frequently cloudy.

We therefore dissolve directly, without washing, in hot nitric acid (1 : 3), or in dilute hydrochloric acid if cobalt or nickel are present, and correct the weight of the oxide subsequently found for the small amounts of lime or magnesia present. It is well to make a qualitative test for these elements in the filtrate from the sulphide. If absent or in small amount the correction in the weight of the oxide may be omitted.

The solution is boiled down rapidly in a casserole, with the addition of nitric acid to expel chlorides. When almost dry the contents are rinsed into a weighed platinum dish or crucible. The evaporation is continued on the water-bath or hot plate until dry, when the nitrate is ignited at the full heat of the Bunsen burner. As some zinc sulphate, which is always present, is not decomposed at this temperature, it is necessary to break up this compound by intense ignition over the blast-lamp. Any lumps should be first broken up by a blunt glass rod. Ammonium carbonate may be used, but is liable to occasion some loss.

It may be possible, by igniting at a low heat, to weigh the zinc as sulphate, after evaporating with sulphuric acid. We are working on this now.

After weighing, the oxide is dissolved in hydrochloric acid, and the small amount of iron always present, thrown down with ammonia, ignited, brushed into the tared watch-glass in the balance, and weighed directly. The filtrate is acidulated with hydrochloric acid, heated to boiling, and tested for sulphates with barium chloride. A slight precipitate will usually form, but this may, in general, be neglected if the ignition has been properly performed. If in weighable amount it may be treated as in the case of the iron, calculated to sulphur trioxide, and, together with the ferric oxide, deducted from the weight of the impure oxide.

If lime or magnesia were present, the filtrate from the iron should be divided into equal parts, one of which is tested for sulphates and the other for lime and magnesia, by throwing out the zinc as sulphide, and testing the filtrate by the ordinary methods. As a rule this is unnecessary unless the lime or magnesia is present in large amounts, for the sulphide is precipitated in dilute solution and the amount of lime remaining in the unwashed sulphide would usually be very small.

The correction for impurities may seem tedious, but in reality it is quickly carried out. Richards has found that zinc oxide obtained by the ignition of the nitrate contains a little occluded nitrogen. This would only amount to a few tenths of a m.grm, and may be neglected unless unusually accurate work is called for.

For the determination of zinc in alloys containing copper, tin, lead, iron, and zinc, dissolve in nitric acid, evaporate to dryness, and take up with nitric acid if tin be present. Filter and separate copper and lead simultaneously by electrolysis. The solution should contain 5 to 10 c.c. concentrated nitric acid in 150 to 200 c.c. water. After removing and washing the electrodes carrying copper and lead, the solution is evaporated to dryness in a weighed platinum dish and the residue ignited and weighed. Dissolve in hydrochloric acid and separate the usually small amount of iron present by ammonia. Ignite, weigh, and deduct from the weight of the zinc oxide. If nickel be present the weight of the combined oxides may be taken and the nickel afterwards determined, when the zinc may be found by difference.

Zinc in pure spelters is best determined by difference. In impure samples it is sometimes more convenient and equally accurate to determine zinc directly. Dissolve ½ grm. in nitric acid and separate the lead electrolytically in a solution carrying 10 per cent nitric acid. Use the platinum cylinder in this case to collect the lead peroxide. Evaporate the solution to dryness in a weighed dish, ignite, and weigh. Dissolve in a little hydrochloric acid, reduce with 2 to 3 grms. granulated zinc, add sulphuric acid to complete the reaction, dilute with ice-water to 1 litre, and titrate with permanganate. Correct for the amount of iron found. If cadmium, arsenic, or other impurities were present in more than traces the above method would be inapplicable unless modified to include treatment by hydrogen sulphide.

We have not found time to make an extended series of tests of this method, but, in numerous analyses of ores and the complete analysis of alloys in which in duplicate analyses the zinc was determined by the well-known methods, the author has convinced himself of the accuracy of the method. — *Journal of the American Chemical Society*, vol. xxi., No. 2, p. 125.

* C. F. McKenna has suggested to the author that the addition of a little paper pulp to the solution prior to filtration will insure a clear filtrate. If some asbestos is stirred into a cloudy zinc filtrate, and the solution passed again through the paper, the filtrate will generally be clear. But in any case the slow washing of the precipitate exposes us to a loss through oxidation.

† The methyl orange used in exactly neutralising the solution prior to the ferrocyanide titration, and which slightly interferes with the delicacy of the end-reaction, may be readily destroyed after the acidulation by pouring into the beaker a little bromine vapour and stirring this in.

LONDON WATER SUPPLY.

REPORT ON THE COMPOSITION AND QUALITY OF DAILY SAMPLES OF THE WATER SUPPLIED TO LONDON FOR THE MONTH ENDING MARCH 31ST, 1899.

By SIR WILLIAM CROOKES, F.R.S.,
and
PROFESSOR DEWAR, F.R.S.

To MAJOR-GENERAL A. DE COURCY SCOTT, R.E.,
Water Examiner, Metropolis Water Act, 1871.

London, April 10th, 1899.

SIR,—We submit herewith, at the request of the Directors, the results of our analyses of the 182 samples of water collected by us during the past month, at the several places and on the several days indicated, from the mains of the London Water Companies taking their supply from the Thames and Lea.

In Table I. we have recorded the analyses in detail of samples, one taken daily, from March 1st to March 30th inclusive. The purity of the water, in respect to organic matter, has been determined by the Oxygen and Combustion processes; and the results of our analyses by these methods are stated in Columns XIV. to XVIII.

We have recorded in Table II. the tint of the several

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samples of water, as determined by the colour-meter described in previous reports.

In Table III. we have recorded the oxygen required to oxidise the organic matter in all the samples submitted to analysis.

Of the 182 samples examined by us during the month, all were found to be clear, bright, and well filtered.

The rainfall at Oxford during the past month has shown a very great deficit. The actual rain that fell was 0·25 inch; the thirty years' average is 1·50 inches. This gives a deficiency of 1·25 inches, changing the previous excess of 0·85 inch into a deficiency of 0·4 inch, or 7·3 per cent on the thirty years' average fall.

Rain fell on six days only, viz., on the 4th, 8th, 21st, 25th, 28th, and 30th. The heaviest fall was 0·08 inch on the 8th.

Our bacteriological examinations of 253 samples have given the results recorded in the following table; we have also examined 44 other samples, from special wells, standpipes, &c., making a total of 297 samples in all:—

	Microbes per c.c.
New River, unfiltered (mean of 25 samples) ..	2032
New River, filtered (mean of 25 samples) ..	35
Thames, unfiltered (mean of 26 samples) ..	12133
Thames water, from the clear water wells of five Thames-derived supplies (mean of 126 samples)	28
Ditto ditto .. .. highest	280
Ditto ditto .. .. lowest	0
River Lea, unfiltered (mean of 26 samples) ..	3977
River Lea, from the East London Company's clear water well (mean of 25 samples) . ..	33

The chief characteristic of the Metropolitan water supply this month has been its exceptional microbic purity. While in February the raw Thames-water contained over 23,000 microbes per cubic centimetre, yielding filtered water containing an average of 54 microbes, the unfiltered Thames in March contained an average of 12,000 microbes, and the filtered water 28 microbes per cubic centimetre. The improvement in the River Lea is equally marked. In February the unfiltered Lea showed an average of 7481 microbes, reduced by filtration to 68; while during March the average number of microbes in the Lea, unfiltered and filtered, have been respectively 5977 and 33. This marked improvement in the river waters is certainly connected with the deficient rainfall of the past month, as detailed in a previous part of this report,

We are, Sir,
Your obedient Servants,
WILLIAM CROOKES.
JAMES DEWAR.

A REVISION OF THE ATOMIC WEIGHT OF NICKEL.*

SECOND PAPER.—THE DETERMINATION OF THE NICKEL IN NICKELOUS BROMIDE.

By THEODORE WILLIAM RICHARDS
and
ALLERTON SEWARD CUSHMAN.

(Concluded from p. 175).

A Brief Criticism of Earlier Work.

THE atomic weights of nickel and cobalt have each been the subject of a score of different researches since the problem was first attacked by Rothoff in 1818. These investigations have not only led to exceedingly discordant results, but have also given rise to several interesting and important controversies. As a chronological list is given in our former papers (*Proc. Amer. Acad.*, xxxiii., 97, 115), there is no need of repeating it here. For the purpose of criticism one should rather classify the investigations according to the methods used in them.

The most direct method of determining the atomic weight of nickel is obviously the reduction of nickelous oxide, for in this way the ratio between nickel and oxygen, the usually accepted standard of atomic weights, is settled at once. Russell; Zimmermann; Mond, Langer, and Quincke; Schützenberger; and Krüss and Schmidt used this method with varying degrees of success.

		Result.
1863	Russell (*Journ. Chem. Soc.*, [2], i., 51)	Ni=58·743
1886	Zimmermann (*Liebig's Annalen*, ccxxxii., 324)	Ni=58·694
1890	Mond, &c. (*Journ. Chem. Soc.*, lvii., 753)	Ni=58·580
1892	Schützenberger (*Comptes Rendus*, cxiv., 1149)	Ni=58·515
1892	Krüss and Schmidt (*Zeit. Anorg. Chem.*, ii., 235)	Ni=57·5 to 64·(!)

Of these five investigations, the third was hastily undertaken only to show that nickel which has been vaporised as nickel carbonyl is essentially similar to the ordinary material; the fourth included only two determinations made with oxide undoubtedly containing traces of sulphate, and the last was hopelessly faulty for reasons already discussed. Hence as exact criteria we may reject these three at once, and turn back to the much more carefully executed work of Russell and Zimmermann.

Russell showed that when the higher oxides of nickel and cobalt are ignited in an inert atmosphere, oxygen is driven off and the monoxide remains. His materials were contained in a Rose crucible of platinum; and after igniting the oxides in a stream of carbon dioxide, he reduced them in a stream of hydrogen. His nickelous oxide was very carefully freed from all extraneous matter except the insidious impurities derived from his glass vessels, against which no precautions were taken. A careful study of his work shows that this is the most serious cause of error likely to affect his final result, but that it was probably in part counteracted by the presence of occluded gases in the oxide; hence we have good reason to believe that this result is probably somewhat, but not much, too high.

Zimmermann followed essentially the same method as Russell. From ten exceedingly concordant analyses he deduced the value 58·694* for nickel—a value slightly lower than Russell's 58·743. His work also was carried out with great care, and the effort was made to avoid the occlusion of alkaline impurities by precipitating the final hydroxide of nickel with pure oxide of mercury, thus doing away with the use of an alkaline precipitant. This improvement also lessened the danger of Russell's other chief error, and at the same time introduced yet another with an opposite tendency—the inclusion of mercury. Hence it is not surprising that his result should be somewhat the lower of the two. An unprejudiced critic cannot but consider Zimmermann's work as the best among the older researches, and it is pleasant to call attention to the fact that Zimmermann's result differs by only the fiftieth of one per cent from ours. The reason why this method gives a result more satisfactory in the case of nickel than in that of cobalt is probably because cobaltous oxide is so much more readily raised to the higher stage of oxidation. Both Russell's and Zimmermann's work may have been slightly vitiated by the presence of occluded hydrogen in their nickel; but it is impossible now to appraise

* Contributions from the Chemical Laboratory of Harvard College. From the *Proceedings of the American Academy of Arts and Sciences*, vol. xxxiv.; No 13, February, 1899.

* Krüss and Alibegoff, who published Zimmermann's result, after his death, unwisely omitted to apply the correction to the vacuum standard. This omission has been supplied above.

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the error involved, because the phenomenon is so irregular.

It is convenient to class together five more investigations which appeared between 1857 and 1871, viz.,—

1857	Schneider (*Pogg. Ann.*, ci., 387; cvii., 616)	58·07
1858	Marignac (*Arch. Sci. Nat.*, Nouv. Sér., i., 375)	58·90
1860	Dumas (*Liebig's Annalen*, cxiii., 25)	59·02
1866	Sommaruga (*Sitzber. Wien. Acad.*, liv., [2], 50)	58·03
1871	Lee (*Am. Journ. Sci.*, [3], ii., 44)	58·01

In the light of present knowledge concerning the possibilities of accurate quantitative work, these contributions may be dismissed with few words. Marignac showed that Schneider's oxalate contained occluded impurities, and Schneider showed that Marignac's chloride could hardly have been both anhydrous and free from oxide. Our own experience entirely confirms both of these criticisms. Dumas's lack of ability to determine chlorine with accuracy throws out his analysis of the chloride at once, even if one is credulous enough to believe that the chloride itself was pure. Sommaruga precipitated sulphuric acid from nickelous potassic sulphate as baric sulphate—a method now ostracised except for crude work. Lee's work was wonderfully accurate considering the small quantities of materials which he used, but these quantities were so microscopic, and his compounds were so complex, that one could not have been expected to improve much upon his error of 1 per cent without a radical reformation of method.

Within this same period appeared another paper by Russell, elaborated as carefully as his previous one, but depending upon a less satisfactory process. The hydrogen evolved by the action of nickel upon hydrochloric acid was measured. Many uncertainties combine to make this method of little value, so that the result (58·77 ?) does not carry with it much weight.

Three chemists in three different decades, Marignac, Baubigny, and Schützenberger, have attempted to solve the question by the quantitative ignition of nickelous sulphate:—

			Greatest difference from mean.
1858	Marignac (*Arch. Sci. Nat.*, Nouv. Sér., i., 374)	Ni=58·70	±0·15
1883	Baubigny (*Compt. Rend.*, xcvii., 951)	Ni=58·73	±0·002
1892	Schützenberger (*Compt. Rend.*, cxiv., 1149)	Ni=58·65	±0·075

The three investigations agreed fairly well upon an average result, 58·71 (Clarke, "Re-calculation," top of page 302), Baubigny's being by far the most satisfactory. This method is one involving two errors which nearly counterbalance each other; the sulphate has a tendency to retain water, while the oxide almost invariably retains sulphuric acid. For this reason, the method gives results which approximate closely to the truth (see "A Table of Atomic Weights," *Proc. Amer. Acad.*, xxxiii., 297; Chem. News, lxxviii., 182). Here, again, we have a support for the conclusion that the value in question cannot be far from 58·7.

All the published work upon the subject has now been referred to, except some early work of Rothoff, Erdmann and Marchand, and Deville (see Clarke, "Re-calculation," p. 291), which deserves no more than a passing mention, and the more recent researches of Winkler. Krüss's misguided work has been sufficiently dissected by Winkler's able but unsparing criticism (*Zeit. Anorg. Chem.*, iv., 10) and in the experimental part of this paper. The only points not covered by Winkler—the rose-coloured flame test and the solubility of nickelous hydrate—are explained in the foregoing pages.

The work of Winkler is surprising in its variety and in the ingenuity of his methods, but unfortunately it is equally surprising in the wide range of 1 per cent between his several results. His earliest work (*Zeit. Anal. Chem.*, 1867, vi., 18; Ni=59·45, Clarke), depending upon the reduction of sodic aurochloride by nickel, giving the extremely high value 59·45, is obviously at fault. Winkler himself ignores it in his discussion (*Zeit. Anorg. Chem.*, iv., 10; viii., 1), so that further criticism of it may well be omitted.

Winkler's two later investigations, carried out only a few years ago, gave results much lower and more satisfactory. In his first revision, he weighed nickel, converted it into chloride, and determined the chlorine both gravimetrically and volumetrically (*Zeit. Anorg. Chem.*, 1893, iv., 10), he wisely regulated his operations in such a way as to avoid the use of alkalis; but in his ardour to escape this danger he encountered others as serious. It is highly unlikely that the electrolytic nickel, dried at only 50° while adhering to the dish, could have been free from impurities, as we have already shown in the experimental part of our paper. Indeed, he confessed in a later paper (*Zeit. Anorg. Chem.*, viii. 4) that the electrolysis of cobalt at any rate is very far from being as accurate a process as it is sometimes supposed to be. The report of the acid reaction of the chlorides of these metals would have had more significance if the indicator had been named, for the salts destroy the magenta of phenolphthalein only because they remove the hydroxyl ions from the solution. Both chlorides are perfectly neutral to methyl-orange. A loss of chlorine during the drying of either chloride would, of course, raise the observed atomic weight; and while in the case of nickel the loss was so small as not to have produced a visible cloudiness, no proof is offered that no loss took place. In the case of the cobalt "eine gewisse, aber so schwache Trübung, dass sie, wie man zu sagen pflegt, nicht 'blank' erschien" involved a loss of as much as 1 per cent of material, and it is well possible that a smaller but still important amount of basic salt may have escaped notice in the case of the nickel. Our own experience with the halides of both metals convinces us that it is quite impossible to obtain them pure and dry by evaporation to dryness in moist air. Turning now to the determination of the chlorine in the salts, we find other grave flaws. No account was taken of the solubility of argentic chloride in the gravimetric work, and several milligrms. must have been washed away by the hot dilute nitric acid used as a washing fluid. One is surprised, too, to find that the antiquated process of burning the filter was adopted, instead of Gooch's admirable substitute. In the volumetric work again the solubility of argentic chloride was overlooked, although it produces a most injurious effect on the method of Volhard (*Proc. Amer. Acad.*, xxvi., 34; and xxix., 67). It is, indeed, surprising to see so eminent a chemist using volumetric methods at all in this way, for everyone knows the difficulty of obtaining results of a very high grade of accuracy by their aid. In this laboratory, the burette is only called into use when at least 99 per cent of the material has been weighed out, and then only a few c.c. of a very dilute solution are added to complete the quota. This is quite a different story. It is evident that nearly all the errors mentioned tend to make Winkler's result too high.

Some singular oversights appear also in the calculation of the results. For example, in one place Winkler compares 0·1662 grm. of nickel with 0·6079206 grm. of silver. The small amount of nickel was deposited in a large platinum dish, and its weight could certainly not have been determined more accurately than within 0·1 m.grm., hence at least three decimal places of the recorded weight of silver were superfluous, even if the volumetric solution could have been prepared with an error of only one part in six millions. It is perhaps well to mention also that his final results, varying in the case of cobalt from 59·5996 to 59·7480 (if O=15·96), are given as far as four decimal places.

While a review of this work is necessary in order to

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explain why the results should be too high, perhaps one should not be severe in one's criticism of it, for Professor Winkler himself rejects it, as well as some later work on cobalt (*Zeit. Anorg. Chem.*, iv., 462), in his most recent contribution upon the subject (*Zeit. Anorg. Chem.*, xvii., 236). In this new paper he pins his faith to another series of determinations made in 1894, with a very ingenious method adopted after sundry fruitless attempts in other directions. It behoves us, then, to consider this later work with great care.

(1894, 1895, Winkler, *Zeit. Anorg. Chem.*, viii., 1291; Ni = 58·85. It must be borne in mind, in referring to Winkler's papers, that he uses the old standard O = 15·96. His values have all been translated into the more convenient notation, O = 16·000, in this paper).

Evidently many of the errors which render the older investigation untrustworthy were eliminated from that of the subsequent year. The nickel was separated from the platinum dish and afterwards ignited in an atmosphere of hydrogen, and the solubility of argentic chloride does not enter into the question. On the other hand, the unfortunate use of volumetric operations and the misuse of figures remained, while to these were added other dangers not present in the older work. The ingenious procedure was as follows: pure nickel was acted upon by pure iodine, and the excess of iodine was determined by sodic thiosulphate. Many text-books upon volumetric analysis name the process of iodometry as one of the most accurate of titrimetric methods simply because the end point is an extremely sharp one. In reality, the lack of permanence of the necessary solutions render it distinctly unsuitable for very accurate work even under the best conditions. When the iodine must remain in solution for twenty-four hours after weighing and before titration, and when this circumstance is complicated by the presence of a metal capable of acting to a slight extent even upon pure water in the presence of air, one can hardly contend that the conditions are the best. The chance of side reactions seems to be too great to admit of infallibility in the results. One is surprised, indeed, that Winkler's results approach as near to those of Zimmermann as they do, and this close approach is evidence of great accuracy of manipulation on Winkler's part. In short, viewed from the standpoint of ordinary analytical experience, Winkler's last work is admirable, while from the standpoint of atomic weight research it is inadmissible. In justice to Professor Winkler it is only fair to add that he realises this fact himself (*Zeit. Anorg. Chem.*, xvii., 239). One need not dwell upon possible inaccuracies, however; for Winkler himself has furnished us with data for computing the error of his method. In a short paper he uses the same method for determining the atomic weight of iron, and finds for this quantity the value 56·174, if O = 16·000 (*Zeit. Anorg. Chem.*, viii., 291). Now, according to the fairly consistent work of Berzelius, Erdmann and Marchand, Svanberg and Norlin, and Maumené, the atomic weight of iron cannot be far from 56·02; and there is no contradictory evidence of serious value.* Winkler's method, then, gave him a result 0·275 per cent† too high in the case of iron, and it is fair to conclude that the error could not have been far different in the case of nickel. Making the corresponding subtraction, Winkler's corrected result approaches astoundingly near to those obtained by Zimmermann and by us.‡

Winkler's corrected value	58·69
Zimmermann's value..	58·694
Richards and Cushman's value ..	58·706
Average	58·70

* Clarke's "Re-calculation," p. 289. The atomic weight of iron is now being further studied in this Laboratory.

† It is possible that a small part of this error is due to the omission of the reduction to the vacuum standard, which would affect the final value by about 0·01 per cent. This correction may have been applied, but there is no evidence of such application.

‡ Mr. Baxter first called our attention to this remarkable unanimity.

Owing to a slight uncertainty in the atomic weight of iron, as well as to the possibility that iron may behave somewhat differently from nickel in iodine solutions, this comparison is less significant than it seems to be; but certainly it does not militate *against* our value for the atomic weight of nickel. It is of interest to note that Clarke's mathematical method of selecting from among the older values led to the number 58·687.

Professor Winkler's sixth and last paper upon this subject appeared only last summer, after the work described in this paper had been completed (*Zeit. Anorg. Chem.*, xvii., 236). In it he kindly points out several possible flaws and omissions in our earlier paper. This criticism will be discussed at length in the next paper on cobalt.

PROCEEDINGS OF SOCIETIES.

CHEMICAL SOCIETY.

Anniversary Meeting, March 29th, 1899.

Professor Dewar, F.R.S., President, in the Chair.

Dr. E. W. Voelcker and Mr. W. P. Bloxam were appointed scrutators, and a ballot was opened for the election of Officers and Council for the ensuing year, the ballot being closed at the conclusion of the President's Address.

The President, in beginning his Address, said that the past two years had been marked by change in the ranks of the active officers of the Society. Last year, Professor Thomson, who had been an Honorary Secretary since March, 1883, resigned office. His services to the Society had been beyond praise, not only from the amount of work actually done, of forethought and care expended, but also from the personal influence which enabled him to discharge the often delicate duties of his office without wounding the susceptibilities of those with whom he had to deal. Dr. Wynne who became Junior Secretary last year, had now resigned the post to take up the arduous duties of Editor of the Society's Journal. Dr. Thorpe, who had been Honorary Treasurer since 1889, vacated the office that day, the eminent services which he has rendered, not only to chemical science, but to the Society, recommending him to the Council for the highest honour the Society had to bestow. Dr. Tilden, who had served the Society twice as Vice-President, would succeed him as Treasurer, and Dr. Scott had been nominated to succeed Dr. Wynne as Secretary. The names of these gentlemen were familiar to the Society as those of persons in every way qualified to discharge the duties of their respective offices.

The Treasurer, as he might still for some minutes call him, would no doubt render them an account of his stewardship, but the duty was incumbent upon him of expressing their deep sense of the debt of gratitude owed him by the Society. During ten years of office, despite the magnificent undertakings of which Dr. Thorpe had been the mainstay, the investments of the Society had increased by one-half, and its income had risen from £4150 to £5286, while, largely owing to his vigilant care, the tendency to an increased expenditure had been kept down to normal proportions.

During his term of office he had had to provide the funds for some very considerable undertakings, chief amongst which were the alterations effected in the meeting room and the introduction of the electric light in 1892, the Society's Jubilee in 1891, and the drawing up of General Indexes to the Society's Journal and the Abstracts from 1873 to 1892. On the completion of this latter piece of work, which Dr. Thorpe would announce to the meeting, it seemed a fitting time to acknowledge the service which the publication of these volumes has

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rendered to everyone interested in the science. They had been issued gratuitously to all Fellows who had received the Journal during the period they cover, provided that application was made for them before December, 1895.

Though the initiative in this issue had been taken by our illustrious colleague, the main burden of the preparation of the index had fallen on a lady, Mrs. Dougal, who edited the two volumes with zeal, energy, and intelligence. He (the President) would wish to bear testimony to her self-sacrificing devotion to this task, which had occupied upwards of five years. It had proved to be one of uncommon and unexpected difficulty. The annual indexing was found to have been done in an irregular and unsystematic way in the past, and much of the work which was understood to be ready to her hand had to be done over again. She had, both directly and indirectly, done the Society a great service—directly, by the compilation which she had executed, and indirectly, by leaving an example of thoroughness and accuracy to her successors. He had also to tender their thanks to the ladies who assisted her, and to Miss Neale, who had taken her place for a short time. The thanks of the Society were also due to the Index Committee, and more especially to Dr. Forster Morley, whose unwearied assistance and experience did much to solve the problems which were daily met with in the progress of the work.

The yearly indexes to the journals had of late shown a tendency to expansion. With a view to making them of more service, a staff of indexers, having a special knowledge of the various departments they undertook, had been engaged.

During the past year the Society was privileged to offer to six of its Past-Presidents its congratulations, and those of the whole scientific world, on the occasion of their completing fifty years' Fellowship of the Society. The Banquet at which they were entertained would long live in their memory. To quote the words of Friedel, "No finer phalanx of the Fathers of our Science exists in any country." The occasion was too recent for him to add anything to the sentiments then expressed. The event, however, was not without a melancholy side. As originally proposed, the foremost of this phalanx would have been their senior Past-President, the last surviving founder of the Society. He would not speak here at length of the services Lord Playfair had rendered to science, but fifty years' active work in the service of the Society required a more special mention. He became a Member of the Council in 1846, in 1850 he was elected a Vice-President, in 1857 he became President of the Society in succession to Professor Miller, and from 1859, for forty years, he remained Vice-President of the Society to which his experience and influence rendered signal service. His last appearance amongst them had been to propose him (Prof. Dewar) as President.

During the past two years the Society had lost by death thirty-six of its Fellows. Lord Playfair was the last survivor of the seventy-seven original members of our Society. In Mr. J. W. Rodger, the Society lost one of the most promising of the younger men of science and a member of its Council. Sir Thomas Dyke Acland had been a Fellow of the Society for over forty years, and though he had never taken an active part in the affairs of the Society, he had rendered great services to our science in its connection with agriculture. Sir Douglas Galton, whose recent loss they had to deplore, had been a Fellow of the Society for a quarter of a century. Mr. Newlands, whose "Law of octaves" has taken an imperishable place in the history of science, was in his fortieth year of membership, and had also served the Society as a Member of Council. His portrait now occupied a place on their walls.

Mr. Groves, who had been connected with the Journal since 1878, first as Sub-Editor, and, in 1884, as Editor in succession to Mr. Watts, resigned office that day. Only those who have been connected with similar publications could measure the full extent of the Society's indebtedness to him, but they could all join the Council in expressing their deep sense of, and thanks for, the important services he had rendered to the Society during those twenty-one years. They could only express the hope that his work for the Society and for science might be continued for many years to come.

Mr. Greenaway, who had for so many years occupied the important office of Sub-Editor, and worked so harmoniously with Mr. Groves, had elected to remain in that position. Dr. Wynne had succeeded Mr. Groves in the editorial chair and could be trusted to preserve that high level of excellence to which the Society's Journal had attained.

The number of papers read before the Society during the past two years was 274, of which 216 had since been published in full in the Society's *Transactions*, the remaining papers being preliminary notices of a more or less temporary character.

The meetings of the Society had been well attended, and the discussions fruitful of interest, but he could desire, in the best interests of the Society, that a larger proportion of the senior members could find it possible to be present.

During the past two years considerable attention had been given by the Council to the question of a suggested revision of the By-Laws. It has been found that no important modification can be made in these without the grant of a new charter, and it is thought that it is hardly worth while to introduce mere verbal changes which might, perhaps, make the meaning of the By-Laws more clear, but which, the council is legally advised, are unnecessary in view of the established practice of the Society.

The next matter of importance which would engage the attention of the Society would probably be the issue of a new catalogue to the Society's Library. Originally founded in 1850, it then consisted of about 270 volumes of journals, 60 miscellaneous volumes, and 100 pamphlets. Its first catalogue was issued in 1851, a second catalogue was prepared by Mr. Watts and issued early in 1861, a third catalogue, now grown from 28 to 112 pages, was issued in 1869, and a fourth, of 138 pages, in 1874. In 1886, a new catalogue, arranged according to subject-matter, was drawn up by Mr. Warington from Mr. Watts's notes, and issued to the Society. It extends to 327 pages, and has an author-index drawn up by Professor McLeod. The catalogue of 1886 contains entries of 5580 volumes of journals, 4223 books, and 1380 pamphlets. Since that time there have been added 3279 volumes of journals, 1361 books, and over 1600 pamphlets. The preparation and issue of this important work would necessarily involve some considerable time and expense to the Society.

One of the great needs of scientific workers is a ready means of acquainting themselves with the bearing and results of general scientific work. The publication of abstracts of particular branches of science is, generally speaking, nearly complete, but there is great overlapping and waste of energy. The suggestion has been made that some change analogous to that recently carried out by the German Chemical Society should be made in the publication of our own abstracts. All such proposals will have the fullest consideration of the Council, but it is clear that it would be unwise to ignore the grave consequences to the financial position of the Society which might result from any too precipitate change in the method of publication of the abstracts. Without entering more fully on this question, he might remark that there was still room for co-operation in this matter between the societies of this country.

They had been asked to co-operate with the American and the German Chemical Society in bringing about an International agreement upon the subject of Atomic Weights. The Council has appointed a Committee to consider the matter.

In the meantime, they had had the opportunity of co-

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operating in the movements designed to honour the memory of two illustrious chemists, Kekulé and Davy; the former by joining in the International Memorial to his memory, the latter by contributing, in conjunction with the Royal Institution and the Royal Society, to a fund designed to restore and preserve the memorial raised over his grave.

The remainder of the Address was of a general and theoretical nature, dealing with recent advances in chemical research, principally in connection with low temperatures.

The numerical strength of the Society was as follows:—

Number of Fellows, March 31st, 1898		2140
since elected		132
reinstated by Council		3
		2275
Removed on account of non-payment of two annual subscriptions	15	
Withdrawn	12	
Deaths	18	
	—	45
Number of Fellows, March 31st, 1899		2230
Foreign Members		38

The following have died:—Sir T. J. Dyke Acland, W. R. Burnett, Michael Conroy, E. Rider Cook, Ramchandra Dutta, George Foord, Sir Douglas Galton, Jeremiah Head, J. G. Heywood, W. L. Hiepe, Charles Lowe, J. A. R. Newlands, Eugen Obach, Lord Playfair, Manning Prentice, H. W. Seely, Matthew Smith, Samuel Spencer.

The number of communications made to the Society during the year was 150.

One hundred and two papers were published in the *Transactions* for 1898, occupying 1047 pages, whereas in the preceding year 114 papers were published, occupying 1204 pages.

The following were the statistics relating to the Abstracts.

	Pages.	No. of Abstracts.
Part I.		
Organic Chemistry	720	1187
Part II.		
General and Physical Chemistry		344
Inorganic Chemistry		284
Mineralogical Chemistry		171
Physiological Chemistry		165
Chemistry of Vegetable Physiology and Agriculture		159
Analytical Chemistry		516
	660	1639
Total in Parts I. and II. ..	1380	2826

Seven hundred and twenty-seven volumes had been borrowed from the Library. The additions comprised 67 books, 285 volumes of periodicals, and 24 pamphlets.

Dr. Gladstone, F.R.S., proposed a vote of thanks to the President, coupled with the request that he would allow his Address to be printed in the *Transactions*.

Dr. Armstrong, F.R.S., seconded the motion, which was carried by acclamation.

The President having returned thanks,

Dr. Thorpe, F.R.S., the Treasurer, in giving an account of the balance sheet, which he laid before the Society, duly audited, said:—

The receipts had been:—By admission fees and subscriptions, £4064; by sale of Journal and advertisements, £740 15s.; and by dividends on invested capital, £428 2s. 1d. The expenses had been:—On account of the Journal, £3007 9s. 10d.; on account of the Proceedings, £287 6s. 10d.; on account of the General Index, £793 16s. 7d.; on account of the Library, £294 19s. 11d.; House expenses, £238 2s. 7d.; the total expenditure being £5415 6s. 8d. Grants amounting to £245 had been made to Fellows from the Research Fund during the year, and a sum of £1316 1s. had been invested in the purchase of £1400 India 2½ per cent Stock.

On laying down his office as Treasurer, to which he was elected in 1889, Dr. Thorpe hoped that it might not be uninteresting to the Fellows if he gave a brief account of the financial progress of the Society during the ten years of his stewardship.

In 1889, the total assets of the Society, excluding the Research Fund, were £12,221; in 1899 they are £17,289.

The total assets of the Research Fund in 1889 were £5464; in 1899 they are £7618.

The aggregate total assets are now £24,907, as against £17,686 in 1889.

In 1889, the total receipts from Fellows were £3402 in 1899 they were £4064, or an increase of 19½ per cent. The annual income from the sale of the Society's publications in 1889 amounted to £365; this year, including an outstanding item on account of advertisements, it is £760, or an increase of £108 per cent. This is due partly to the increased circulation of the Journal and partly to the increased price which can be obtained for it. The advertisements now bring in an income equivalent to about £2000 of funded property.

The total income of the Society from all sources in 1889 including the balances at the bank was £5824; at the close of the present financial year it has amounted to £7180.

It will be seen, therefore, that whilst the receipts from the Fellows have increased by 19½ per cent, the income of the Society has increased by 23·3 per cent, and the total assets, some of which may be counted upon to still further increase the annual income, have increased by 40·8 per cent.

But if it may be said of societies, as of individuals, that their riches consist, not in the abundance of their possessions, but in the fewness of their wants, it is the experience of the Treasurer that the Chemical Society is by no means a rich corporation, for its wants advance, almost *pari passu*, with its possessions. His successor would find that, however ingenious he may be in securing money, the Society, with equal or with even greater ingenuity, will find a method of relieving him of it.

He regretted to find that he had—he hastened to add, by direction of the Council—signed cheques for a greater amount than any one of his predecessors. During the ten years he had been in office, he had disbursed nearly £45,000 of the Society's money. In explanation of this, he might point out that the annual cost to the Society of its publications has steadily increased since 1889. In that year the expenses connected with its publications came to £2565; this year, in spite of a considerable saving in the printer's bills, and in spite of the draconian methods of the Publication Committee, its publications, excluding the Collective Index, have cost £3370.

The expenses on account of the Library also steadily increase. In 1889, £196 was spent in books, periodicals, and binding; this year, which has been somewhat below the average of the preceding years, the amount has been £246.

The House expenses in 1889 came to £184; this year they are £238.

The total expenditure in 1889 was £3430; this year it has been £5415.

As regards these disbursements, he might be pardoned, perhaps, for pointing out that none of his predecessors had been called upon to spend so large an amount of the Society's money in what might be termed extraordinary expenditure. To begin with, his immediate predecessor handed him over—and it was his only legacy—certain applications for increase of salary on the part of the Editorial staff, and he was good enough to urge that he

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should deal with them liberally. The liberality has resulted in a difference of £1000 to the Society.

In 1891, the Society celebrated its Jubilee, at a cost, notwithstanding the generous assistance of the Goldsmiths' Company, of about £450. In the following year, the alteration of the meeting room and the installation of the electric light was taken in hand, at a cost of £1490.

Shortly afterwards, the Society was called upon to provide for the declining years of an old and faithful servant. There was no circumstance connected with his official career as the Treasurer of the Society which he recalled with greater pleasure than its action in regard to Mr. Josiah Hall's pension.

In the early part of 1894, the Society determined to print a Collective Index of its publications from 1873 to 1892. This has proved to be even a more formidable undertaking than was expected. It has occupied nearly five years in execution, and has cost some £1740. It is now happily completed, and the Society may congratulate itself upon possessing an adequate key to the great store of chemical knowledge which it has accumulated during twenty years.

The revision of the annual indexes necessitated by this great work has shown the absolute need for their more systematic preparation. This has led to the establishment of a special staff of indexers, at an annual cost to the Society of upwards of £60.

Another item of expenditure which had arisen during his tenure of office is connected with the lectures which are given in memory of the deceased Foreign Members. The Society has now a collection of eight of these Memorial Lectures, all of which have been given gratuitously by Fellows or friends on the invitation of the Council. Their publication has cost about £400. These lectures together constitute a most valuable record of contemporary chemical history, and it is hoped that, as the Council have directed, they may be issued in a separate volume, with the accompanying illustrations, before the end of the next financial year.

In their donations to funds connected with the illustrious names of Lavoisier, Davy, Stas, Kekulé, Cannizzaro, the Fellows have not been unmindful of their obligations to these great pioneers in chemical enquiry, nor have they been forgetful, as the gathering of last November showed, of their obligations to the pioneers in their own Society happily still amongst us.

The account-books of the Society show that what he had called the extraordinary expenditure which has been incurred during the last ten years is close upon £7000.

He thought, however, they would all feel that, in the enhanced position of their Society, in the greater comfort and convenience of their meeting-room, in the improvement and increased value of their publications, they had had an abundant return for this expenditure. Although but for it he might have been able to add a few more thousand pounds to their capital account. He hoped the Fellows would not hold him responsible for this omission, but look with a lenient eye upon the financial transgressions of what he sometimes felt himself to have been —a too compliant purse-bearer.

Mr. David Howard proposed that the thanks of the Fellows be tendered to the Treasurer for his services during the past year; this motion was seconded by Mr. F. J. M. Page, and carried.

The Treasurer, in responding, proposed a vote of thanks to the auditors.

Prof. Hodgkinson seconded the motion, which was unanimously adopted, and acknowledged by Prof. Tilden on behalf of Dr. Horace Brown.

Dr. E. W. Voelcker proposed a vote of thanks to the Officers and Council.

Mr. H. B. Baker seconded the motion, which was unanimously adopted.

Prof. Dunstan, F.R.S., responded on behalf of the Council.

Prof. Thomson, F.R.S., proposed a vote of thanks to the Editor, Sub-Editor, Abstractors, and Indexers, which was seconded by Dr. Messel, and carried.

Mr. Groves, F.R.S., responded.

The scrutators having presented their report to the President, he declared that the following had been duly elected :—

President—T. E. Thorpe, Ph.D., D.Sc., LL.D., F.R.S.

Vice-Presidents who have filled the office of President—Sir F. A. Abel, Bart., K.C.B., D.C.L., F.R.S.; H. E. Armstrong, Ph.D., LL.D., F.R.S.; A. Crum Brown, D.Sc., LL.D., F.R.S.; Sir W. Crookes, F.R.S.; James Dewar, M.A., LL.D., F.R.S.; Sir E. Frankland, K.C.B., D.C.L., F.R.S.; Sir J. H. Gilbert, Ph.D., LL.D., F.R.S.; J. H. Gladstone, Ph.D., D.Sc., F.R.S.; A. Vernon Harcourt, M.A., D.C.L., F.R.S.; H. Müller, Ph.D., LL.D., F.R.S.; W. Odling, M.B., F.R.S.; W. H. Perkin, LL.D., Ph.D., F.R.S.; Sir H. E. Roscoe, LL.D., F.R.S.; W. J. Russell, Ph.D., V.P.R.S.; A. W. Williamson, LL.D., F.R.S.

Vice-Presidents—C. E. Groves, F.R.S.; G. D. Liveing, M.A., D.Sc., F.R.S.; T. Purdie, Ph.D., F.R.S.; William Ramsay, Ph.D., LL.D., F.R.S.; J. Emerson Reynolds, M.D., D.Sc., F.R.S.; John M. Thomson, F.R.S.

Secretaries—Wyndham R. Dunstan, M.A., F.R.S.; A. Scott, M.A., D.Sc., F.R.S.

Foreign Secretary—Raphael Meldola, F.R.S.

Treasurer—William A. Tilden, D.Sc., F.R.S.

Other Members of Council—H. Brereton Baker, M.A.; E. J. Bevan; Frank Clowes, D.Sc.; H. J. H. Fenton, M.A.; W. Gowland; C. T. Heycock, M.A., F.R.S.; D. Howard; Rudolph Messel, Ph.D.; G. T. Moody, D.Sc.; H. Forster Morley, M.A., D.Sc.; Arthur Smithells, B.Sc.; James Walker, D.Sc.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

Note.—All degrees of temperature are Centigrade unless otherwise expressed.

Comptes Rendus Hebdomadaires des Séances, de l'Académie des Sciences. Vol. cxxviii., No. 13, March 27, 1899.

Preparation and Properties of Crystalline Calcium Phosphide.—Henri Moissan.—The reduction of tricalcic phosphate by carbon gives, under certain conditions, a crystalline phosphide of calcium, of a dark red colour and having the formula P_2Ca_3. The most curious reaction of this new compound is the facility with which it decomposes cold water, forming calcium hydrate and phosphoretted hydrogen. It may be remarked that a great number of binary compounds of calcium have this curious property of decomposing cold water and forming a hydrated oxide and a gaseous compound of hydrogen united with the other element of the binary compound. Calcium hydride decomposes cold water with evolution of hydrogen, calcium carbide with evolution of acetylene, whilst calcium nitride gives the same reaction with formation of ammonia.

Properties and Applications of Aluminium.—A. Ditte.—The author has continued his researches on aluminium, more especially with regard to certain alloys of aluminium used in objects of military equipment. In the various alloys examined, he finds the aluminium is attacked very easily, being protected, as in the unalloyed state, by thin layers of fatty matter, &c., which, on being decomposed by alkaline matter, again exposes the surface of the aluminium to the action of other reagents.

Decomposition of Carbonic Oxide in presence of Metallic Oxides.—O. Boudouard.—This paper gives an account of the continuation of the author's work on the decomposition of carbon monoxide by metallic oxides. He has now continued his researches up to a temperature

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of 650°. He finds that the reaction of the decomposition of carbonic oxide is a function of the time, and it depends also on the quantity of metallic oxide present. The quantity of carbonic acid formed increases in a regular manner, but whilst at 445° the decomposition of the carbonic oxide is total, at 650° it is limited. Experiments made in the presence of oxide of cobalt show that the reaction stops when the gaseous mixture contains 61 per cent of CO_2 and 39 per cent of CO.

Decomposition of Carbonic Acid in the presence of Carbon.—O. Boudouard.—The author examines the reaction $CO_2+C=2CO$ from a quantitative point of view at various temperatures, the first series of experiments being made at 650°. Glass tubes are used, in which the carbon is placed; the tubes are then filled with carbon dioxide and sealed. They are now heated for lengths of time varying from eight minutes to twelve hours. The proportion of CO_2 and CO is then measured. The decomposition of the carbonic acid gas at this temperature is never total, but it is curious to remark that the limiting proportion is the same as that found in examining the decomposition of carbonic oxide (61 per cent CO_2 and 39 per cent CO).

Dissociation of Mercuric Oxide.—H. Pélabon.—The author has studied the dissociation of mercuric oxide by finding the state of equilibrium of a system consisting of oxide of mercury, oxygen, and liquid mercury when a fixed temperature is maintained for a sufficiently long time. In this case, the thermodynamical theory of dissociation indicates that the tension of the oxygen in the system is a function of the temperature only, and depends neither on the mass of oxide of mercury, nor on the mass of the mercury contained in the system, and the author's experiments verify this result between the temperatures 440° and 620°. In the case when the system under examination does not contain liquid mercury at the temperature of the experiment, the tension limit of the oxygen depends on the value of the vapour-tension of mercury. The author has examined the particular case when the oxygen and mercury vapour are mixed in equivalent proportions, and has determined for each value of the temperature the tension-limit of the oxygen. The numbers obtained allow of a verification of a consequence of the theory of dissociation, by showing that, in this case, the product of the pressure of the oxygen by the square of the vapour-pressure of mercury is a positive number, of which the value depends on the temperature only.

Action of Bis-diazoic Chlorides of Benzidine, Ortho-tolidine, and Dianisidine on Ethyl and Methyl Malonates.—G. Favrel.—In the author's first experiments he uses a method analogous to that by which he has already prepared dihydrazones of cyanacetic ethers and acetylacetone. He obtains, in the presence of an alkali, a reddish yellow precipitate insoluble in excess of alkali, which, after desiccation, easily decomposes on a very slight rise of temperature. By reason of its instability, the product cannot be obtained crystalline or analysed. Much better results are obtained when acetic solutions are used. Yellow crystals are then obtained, melting at 178—180°.

Berichte der Deutschen Chemischen Gesellschaft.
Vol. xxxi., May 23, 1898.

The Oxidation of *p*-Nitrotoluenesulphonic Acid.—A. G. Green and A. R. Wahl.—It has been suggested that the acids already described by the authors (dinitrodibenzyldisulphonic and dinitro-stilbene-disulphonic) were not really free acids, but the acid salts of sodium, and that the latter contained one molecule of oxygen less than it should. To decide this point definitely, the authors have determined by analysis the quantity of zinc necessary to reduce the disodic salt of dinitro-stilbene-disulphonic acid, and they found that the figures corresponded very closely with those required by the formula they proposed and still consider correct, viz., $C_{14}H_{10}N_2S_2O_{10}$.

A New Method of Preparing *a*-m-Xylylsulphamic Acid.—A Junghahn.—By heating the crystalline mass formed by passing dry sulphurous acid through *a*-m-xylidine, in a sealed tube for five hours at 170—180°, the author obtained, from 30 grms. of xylidine, about 10 grms. of a compound which appeared to be the xylidine salt of *a*-m-xylylsulphamic acid formed according to the equation—

$$4C_6H_3\overset{(CH_3)_2}{\underset{NH_2}{<}}+3SO_2=$$

$$=S+2\left(C_6H_3\overset{(CH_3)_2}{\underset{NH.SO_3H.C_6H_3}{<}}\overset{(CH_3)_2}{\underset{NH_2}{<}}\right)$$

Iodochloride of Phenyl.—F. Keppler.—Iodochloride of phenyl is decomposed at the end of two months in the dark, one month in diffused light and a few hours in direct light in a closed vessel forming *p*-chloro-iodobenzene, fusible at 55—56°. It can, however, be kept in an open exsiccator by taking certain precautions.

Action of Sulphochloride of Phosphorus on the Aqueous and Alkaline Solutions of the Phenols.—W. Autenrieth and O. Hildebrand.—Sulphochloride of phosphorus, $SPCl_3$, acts readily, and generally in the cold, on the monovalent phenols and their substitution products, in aqueous and alkaline solution. Substances are formed corresponding to the general formulæ $SP(OR)_3$, $SP(OR)_2Cl$, $SP(OR)Cl_2$, in which R represents an aromatic residue. These compounds are insoluble in alkalis and are deposited immediately during the reaction. Acids of the formula $SP(OR_2)OH$ are also formed, and are found in the aqueous solution in the state of sodic salts. Sulphochloride of phosphorus may be considered as a reagent for the monovalent phenols and their substitution products; by its aid we can introduce into their molecules the inorganic radicals (SP)‴, (SPCl)″, and $(SPCl_2)'$.

The Synthesis of a Phosphazine.—W. Autenrieth and O. Hildebrand.—The authors find that by heating together the monophenoxylised sulphodichloride of phosphorus and *o*-phenylenediamine, the reaction takes place in two phases. It is probable that in the first phase one atom of chlorine is eliminated from the dichloride at the same time as one atom of hydrogen is eliminated from one of the "amido" groups of the *o*-phenylenediamine to form chlorhydrate of diamine, and an intermediate product which has not yet been isolated. On then heating to 170° the formation of a nucleus takes place with the elimination of hydrogen:—

$$SP\begin{cases}OC_6H_5\\NH\\(ClH)NH\end{cases}>C_6H_4=HCl+PS\begin{cases}OC_6H_5\\NH\\NH\end{cases}>C_6H_4.$$

The *p*-thiophenoxylphenphosphazine thus obtained crystallises in alcohol in fine prisms, melting at 185°; they are almost insoluble in cold water, slightly so in warm water, and easily in alcohol, ether, &c.

Synthesis of Aromatic Aldehydes.—L. Gattermann.—Starting from the supposition that prussic acid or certain of its derivatives might exist in the tautomeric form C=NH, the author presumed that aromatic bodies might be added to it in the presence of chloride of aluminium, in the same manner as carbonic oxide. Research has confirmed this idea, and the author has prepared, by means of anisol, phenetol, and the cresol ethers, the corresponding aldehydes with almost quantitative returns.

Formation of Acetohydroquinone by means of Acetaldehyde and of Benzoquinone under the Influence of Sunlight.—H. Klinger and W. Koldenbach.—The authors have prepared acetohydroquinone,—

$$CH_3CO.C_6H_3(OH_2),$$

by submitting a mixture of benzoquinone and freshly distilled acetaldehyde in a sealed tube to the prolonged action of direct sunlight. This compound sublimes in long needles of a greenish yellow colour, melting at 202°; it is soluble in soda-lye, ammonia, or a solution of carbonate

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of soda, giving an intensely yellow colour; acids re-precipitate it from these solutions. Its dibenzoate, $CH_3CO.C_6H_3(OCO.C_6H_5)_2$, prepared by means of chloride of benzoyle, crystallises in alcohol and benzene in prisms melting at 113°; the corresponding phenylhydrazone occurs in brilliant straw-coloured needles, fusible at 148°.

On some Perhaloïds.—A. Samtleben.—The author has examined the action of halogens on the tertiary amines of the benzene series, as well as on some acetonic cyclic bases. When bromine, iodine, or chloride of iodine is made to react on the free tertiary bases of the aromatic series, substitution products are formed; but if we cause them to react on the chlorhydrates, bromhydrates, or iodhydrates of the above-mentioned bases, coloured products of addition are generally formed. In nearly every case compounds are formed having the general formula $R.H.X-X_2$, in which R = a tertiary amine and X an atom of a halogen. The perhaloïds may be represented by the following formulæ.—$R.HCl.ClI$; $R.HBr.Br_2$; $R.HI.I_2$.

Ethyltriamidonaphthalene and its Acetyl Derivative.—O. Markfeldt.—The author has prepared ethenyltriamidonaphthalene by the reduction of dinitroacet-a-naphthalide by means of iron and hydrochloric acid, and has studied the nitric colouring-matters derived therefrom, of which some appear to be of interest The acetyl derivative was obtained by the usual method, starting with the chlorhydrate; its acetate crystallised in white flakes, fusible above 280°; it contains 3 molecules of acetic acid, two of which are in the form of acid of crystallisation.

$$C_{10}H_5\begin{cases}NH\\ N\geqslant C.CH_3\\ NH.C_2H_3O\end{cases}.CH_3COOH+2CH_3.COOH.$$

The acetyl base itself crystallises in silky needles, difficultly soluble in cold water, fusible above 280°, and containing 2 aqua. The author also describes the chlorhydrate of the acetylised derivative, the sulphate, nitrate, and picrate.

Indigo Oxime.—J. Thiele and R. H. Pickard.—When indigo is treated with an alkaline solution of hydroxylamine it dissolves very easily, giving a monoxime; but the dioxime cannot be obtained even with a large excess of hydroxylamine. This oxime crystallises in alcohol in violet-brown coppery needles, melting with decomposition at about 205°.

MISCELLANEOUS.

Thorium Nitrate.—This chemical has suffered an enormous fall in value during the past year. At the commencement of 1895 the nitrate was selling for 1800 m. to 1900 m. (£90 to £95) per kilo. To-day it can be obtained for 37 m. per kilo. This strikingly rapid fall in price is due, not to competition, but to a change in the raw material used and in the method of manufacture. In 1895 the costly Norwegian thorite was used, and to obtain 1 kilo. of thorium nitrate 800 m. to 900 m. had to be expended upon raw material. The monazite, which is now alone used at the starting-point of the manufacture, was not a marketable article in 1895. The production of thorium nitrate three years ago was also a mere fraction of that of the present day, and, as usual, the increased scale of manufacturing operations has tended to cheapen the cost per kilo. The present prices are, however, too low to render the manufacture, as carried on to-day, profitable.—*Chemist and Druggist.*

A New Indicator for Acidimetry and Alkalimetry.—Em. Riegler.—A solution of guaiacal in alkali, mixed with a solution of diazoparanitraniline, gives a coloured diazo-body of the formula $C_6H_4—NO_2—N=N—C_6H_3O.CH_3.OH$. This body, which is brown, is soluble in alcohol and insoluble in water. The indicator is obtained by dissolving 0·2 gr. of the above compound in 100 c.c. of alcohol. One or two drops of the solution give with alkalis a beautiful red coloration. The slightest excess of acid changes the colour to greenish yellow. The sensitiveness of this indicator is greater than that of phenolphthalein. To prepare the diazo-body, 1 grm. of guaiacol is dissolved in 50 c.c. of water to which has been added 30 c.c. of a 10 per cent solution, and into this a solution of diazonitraniline is introduced, prepared as follows:—1·25 grs. paranitraniline, 50 c.c. distilled water, and 4 c.c. concentrated hydrochloric acid are placed in a flask, which is warmed until solution is complete. 100 c.c. of cold water is then added, and, when the mixture is cool, 0·5 gr. sodium nitrite in about 30 c.c. of water. In mixing this solution with that of the guaiacol, a red liquid is obtained, from which the insoluble coloured body is precipitated by acidifying with strong sulphuric acid, added drop by drop. The precipitate is washed, and dried in a desiccator over sulphuric acid.—*Bulletin de la Société des Sciences de Bucarest, Roumania*, 1898, No. 6.

MEETINGS FOR THE WEEK.

MONDAY, 24th.—Society of Arts, 8 (Cantor Lectures). "Leather Manufacture," Prof H. R. Procter, F.I.C.
—— Society of Chemical Industry, 8.30. "The Relations of the Society to Chemical Engineering and to Industrial Research," by George Beilby.
TUESDAY, 25th.—Royal Institution, 3. "Zebras and Zebra Hybrids," by Prof. J. Cossar Ewart, M.D., F.R.S.
WEDNESDAY, 26th.—Society of Arts, 8. "Coal Supplies," by T. Forster Brown.
THURSDAY, 27th.—Royal Institution, 3. "The Atmosphere," by Prof. Dewar, M.A., LL.D., F.R.S.
—— Society of Arts, 4.30. "Judicial Reform in Egypt," by Sir John Scott, K.C.M.G., D.C.L.
FRIDAY, 28th.—Royal Institution, 9. "Some Features of the Electric Induction Motor," by Prof. C. A. Carus Wilson, M.A., M.Inst.C.E.
SATURDAY, 29th.—Royal Institution, 3. "Machiavelli," by Louis Dyer, M.A.

BRITISH ASSOCIATION FOR THE ADVANCEMENT OF SCIENCE,

BURLINGTON HOUSE, LONDON, W.

The NEXT ANNUAL MEETING of the ASSOCIATION will be held at DOVER, commencing on WEDNESDAY, SEPTEMBER 13, 1899.

PRESIDENT-ELECT:

Prof. MICHAEL FOSTER, M.D., D.C.L., LL.D., Sec.R.S.

Notice of Papers proposed to be read should be sent to the Office, Burlington House, before JULY 1.

Information about local arrangements may be obtained from the LOCAL SECRETARIES, Castle Hill House, Dover.

G. GRIFFITH, Assistant General Secretary.

MASON UNIVERSITY COLLEGE, BIRMINGHAM.

FACULTY OF SCIENCE.

RESEARCH SCHOLARSHIPS.

(Founded by the late T. AUBREY BOWEN, Esq., of Melbourne, Australia).

(*a*) Two BOWEN SCHOLARSHIPS in ENGINEERING, each of the value of about £96.
(*b*) One BOWEN SCHOLARSHIP in METALLURGY, of the value of about £96.
(*c*) Three PRIESTLEY SCHOLARSHIPS in CHEMISTRY, each of the value of about £96.

The object of these Scholarships is to encourage higher work and research in Scientific Professional Engineering and in Chemical and Metallurgical Science.

Applications, supported by details of educational training, and references to former teachers and others, should be sent to the Registrar on or before the 1st June, 1899. The awards will be made in September next, and the Scholarships will be tenable during the Session 1899-1900.

Further particulars may be obtained on application to the REGISTRAR.

Mr. J. G. LORRAIN, M.I.E.E., M.I.M.E, M.S.C.I.,

Fellow of the Chartered Institute of Patent Agents,

NORFOLK HOUSE, NORFOLK STREET, LONDON, W.C.

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THE CHEMICAL NEWS.

VOL. LXXIX., No. 2057.

IRON SEPARATIONS WITH ALKALINE SALTS.

FIRST PAPER.

By HARRY BREARLEY.

FOR the separation of iron from manganese, zinc, nickel, cobalt, and in some cases copper, the most commonly used reagents are alkaline acetates and phosphates in a more or less acetic acid solution. Occasionally, though less now than formerly, sulphates are also used.

Any proposed reagent must obviously form an insoluble compound with iron, either in the cold or by subsequent heating. In view of the fact that ferric solutions may be "neutralised"—*e.g.*, arranged so that a small fraction of the original solution of the salt holds most of the iron dissolved as hydrate, $Fe_2Cl_6.8Fe_2(HO)_6$—it is permissible to use reagents which form comparatively unstable compounds, and whose use for precipitating "unneutralised" solutions of ferric chloride is not satisfactory. The value of such a reagent is illustrated by a former paper, "Separations with Alkaline Chromates" (CHEM. NEWS, lxviii., 14).

Some available reagents are alkaline acetates, phosphates, sulphates, chromates, tungstates, and molybdates. The object of these papers is to present the essential features of the commoner reagents, the principles on which they are based, and the limits within which they should be used. Chromates, molybdates, and tungstates, particularly the two latter, require more detailed treatment. At present their possibilities are unknown, and we cannot say what special features they may have; they have at least *the* essential property—they form insoluble compounds with iron.

The Separation as Acetate.

A former series of articles on "Separations with Alkaline Acetate" (CHEM. NEWS, vols. lxxv. and lxxvi.) makes it unnecessary to discuss here the merits and demerits of this very common reagent at any great length. I am induced to include it in this series for the sake of completeness, and to afford myself an opportunity of making known certain additional facts concerning its use.

The following experiments, amongst others, are the [illegible] a criticism of the latter portion of the method [illegible]ng iron and nickel described in Arnold's "Steel [illegible]alysis," page 163. This method is typical of [illegible] of alkaline acetates for the above purpose, [illegible] such meaning is read into the words as they [illegible]erly convey, it cannot give accurate results. [illegible]e of error lies in the enormous excess of acetate [illegible]fect is supposed to be compensated for by adding [illegible] *the cold solution*, and then raising the mixture [illegible]. This instruction originated with Wollcott [illegible]bbs (CHEM. NEWS, xi., 102), and has been repeated and sworn by over and over again. Personally I have for some time had little respect for this cumbersome detail, having previously shown that other abuses of the acetate separation being avoided, the separation was as satisfactory with as without it. I have now to show that the advantage claimed for it is an unreal one,—that, in fact, it is a harmful as well as a troublesome modification.

I have chosen the separation of iron and nickel to illustrate the question generally, because that element is more difficult to separate than any of the other elements for which acetate is commonly used. The points elucidated should, however, be taken as applying with greater or less force to the separation of iron from manganese, zinc, cobalt, or copper.

Four grms. of iron along with [illegible] grm. of nickel were dissolved in hydrochloric and oxidised with nitric acid, partially neutralised, and divided into four equal portions. After dilution to c.c. of strong ammonium acetate was added, in drops and with vigorous shaking, to each at the indicated temperatures. The figures are grms. of nickel recovered. The series shows unmistakably that the addition of acetate to the cold solution is the very worst time at which it could be made.

Temperature.	Grms. Ni recovered.
Cold (16° C.)	0·0833
60° C.	0·0863
80° C.	0·0910
Boiling	0·0947

This result was anticipated, on the following grounds, some time before an opportunity occurred of testing the point experimentally.

A large excess of acetate always leads to an imperfect separation. This arises from the fact that—

1. The excess of acetate transforms the nickel as well as the iron salts into acetates.
2. *Along with* the decomposition of the ferric acetate the nickel is also partially decomposed.

A separation of iron and nickel is therefore influenced by two factors—the excess of alkaline acetate and the decomposing ferric acetate.

When the acetate is added to the cold solution both these factors exert their maximum influence. On adding acetate to the boiling solution the first portion of it precipitated the iron; when the remaining portion is added the conditions are changed: now the iron is present in suspension only, and its influence is greatly lessened.

This is an important point. Previous experiments have shown that the use of minimum acetate leads to the perfect separation of iron and nickel; but the excess which could be used without causing an imperfect separation has been represented as being very small. This because, in the experiments made to test the matter, [illegible] acetate, for the sake of uniformity, was added to the c[illegible] solution.

The acetate separation, as we have previously describ[illegible] it, has been subject to the criticism—not a very serious one—of disallowing the free and easy use of the precipitant: this criticism is tempered somewhat, if it be understood that the acetate is to be added slowly to the boiling solution. By way of comparison the figures of column I. are reprinted from CHEMICAL NEWS (lxvi., 224), under precisely such circumstances as were then arranged, except that the acetate was added to the boiling solution; we now obtain the figures of column II.

Dilute* am. acetate.	Per cent Ni recovered. I.	II.
10 c.c.	100	—
20 ,,	99·0	99·8
50 ,,	95·2	98·1
100 ,,	90·0	94·8

* 75 c.c. strong acetate made up to a litre.

It is pleasing to find that the most convenient conditions —addition of acetate to the hot solution—should be also the most desirable in point of exactness.

Two other points generally insisted on are that a separation increases in exactness as the iron decreases, nickel being constant, and similarly iron being constant, the separation is better for small than large amounts of nickel, assuming, of course, that the circumstances are otherwise the same so far as amount of acetate used, volume of solution, &c., are concerned.

The former of these two conclusions is by no means obvious if we bear in mind the *rationale* of an acetate separation. As a matter of fact the separation may be better or worse, or equally good.

Suppose our solutions of nickel containing varying amounts of iron are all completely neutralised, there will

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be the greatest amount of iron existing as ferric chloride in those samples containing the most iron: this means that more ammonium acetate will be needed to convert it into $Fe_2(C_2H_3O_2)_6$, and (the same amount of acetate being added to each sample) consequently the excess of acetate, which alone is harmful, will be less. And again, in the hot solution the $Fe_2(C_2H_3O_2)_6$ is decomposed and free acetic acid is liberated. Both these changes are favourable to improving separations, and they may be made so great as to afford a better separation from two than from two-tenths grms. of iron.

Here, as before, the matter is most easily settled by arranging relatively imperfect separations through the use of large amounts of acetate. The experimental details are—Nickel 0·1 grm., varying iron, perfect neutralisation, 10 c.c. acetic acid each assay, volume of solution precipitated from about 500 c.c. and 10 c.c. strong* ammonium acetate added to the cold solution.

Iron added.	Ni recovered.
2 grms.	0·0932
1 grm.	0·0884
0·5 „	0·0897
0·2 „	0·0916
0·05 „	0·0954

The second conclusion, viz., that with increasing amounts of nickel, iron being constant, the separations are less exact, seems more likely to be generally true. The absolute amount of nickel lost may be greater where the amount of nickel present is greater. It has yet to be shown that the percentage loss varies in the same direction.

ELECTROLYTIC SEPARATION OF COPPER FROM MERCURY, AND OF COPPER FROM ARSENIC.

By N. REVAY.

I. *Separation of Copper from Mercury.*

A. *Precipitation in Acid Solution.*—Although Freudenburg claims to have separated mercury from copper in acid solution, the author has not succeded in obtaining satisfactory results by this method. The electrolysis was conducted with the greatest care, and strictly according to the conditions laid down by Freudenburg, but without success.

B. *Electrolysis of the Solution of Double Oxalates.*—This method is already known, and gives good results. It is therefore not necessary now to describe it.

C. *Electrolysis of the Solution of Double Cyanides.*—This method has given good results to Smith and Freudenburg; but Smith and Frankel were unable to effect a complete separation when the proportion of copper present was greater than 25 per cent. This is due to the fact that the difference of potential between mercury and the solution of its cyanide varies considerably with the concentration of the liquid. According to Werner and Bolton the polarisation is greater as the number of ions of mercury present is smaller. By using 0·5 to 0·6 grm. of crystallised sulphate of copper, and quantities of mercuric chloride varying from 0·25 to 1·0 grm., and adding 3 grms. of cyanide of potassium, the author has found the following proportions of mercury in the mercuric chloride:—1, 73·60; 2, 73·75; 3, 73·73; and 73·76; the theoretical proportion being 73·80 per cent. These results were obtained with an electromotive force of 1·8 to 1·9 volts, and the mercury obtained was perfectly free from copper,

II. *Separation of Copper from Arsenic.*

To effect this separation it is necessary to work under such conditions that the copper will be deposited on the cathode and the arsenic on the anode. The conditions are easily arranged when the arsenic exists in the solution in the state of an anion (as in arseniate of potassium, for example), and is not easily transformable into a compound in which it would play the part of a cathion. We can use an acid, ammoniacal, or cyanide solution, with an electromotive force of 1·6 to 1·8 volts. If the difference of potential is too high, the arsenic is partly precipitated at the cathode in the form of a grey powder, probably by reason of the reduction of the pentavalent arsenic to the trivalent form. This takes place specially when the trivalent arsenic is susceptible of forming a salt with the acid ion (in hydrochloric solution, for example). This transformation is less easy in nitric solution, and still less so in sulphuric solution. It is therefore preferable to work in sulphuric solution. Cyanogen has very little tendency to form a salt with arsenic; electrolysis can, therefore, be just as easily effected in a double cyanide solution. Good results have also been obtained in ammoniacal solution.—*Zeitschr. für Electrochemie*, iv., 329.

* By neutralising 0·830 ammonia with 33 per cent acetic acid.

THE ANALYSIS OF GLUE.

By RICHARD KISSLING.

Two new methods have recently been proposed for the analysis of glues. Stelling (*Chem. Zeit.*, 1896, xx., 461) recommends the estimation of the non-gluey material; Fels (*Chem. Zeit.*, 1897, xxi., 56) proposes estimating the viscosity of a solution of the glue.

I have made a number of experiments to determine the relative values of these two methods, and I propose to record briefly the results I have obtained.

Stelling's process consists of adding to a solution of glue (1 part of glue to 4 parts of water) alcohol at 96°, in small quantities at a time, while constantly stirring (we take 15 parts of glue and 60 parts of water, and make up to 250 c.c. with alcohol).

We then determine the proportion of non-gluey matter present, by evaporating down an aliquot part of the alcoholic solution, previously filtered, and weighing the residue. This process is thus based on the supposition that alcohol at about 72 per cent in volume leaves the glutine intact, while it dissolves the products of decomposition, considered as non-gluey material.

I should here remark that the products meant by the term "non-gluey" should not be considered as products of decomposition of the glutine; they are also found in the original solution of glue, before it has undergone any destructive process by evaporation. I would also remark that the supposition that alcohol at 72 per cent is best for separating the glutine from the products of decomposition does not rest on any theoretical considerations, and if we proceed exactly according to Stelling's instructions this separation does not even take place.

Glutine is not entirely insoluble in alcohol at 72 per cent, inasmuch as, on evaporating down the filtered alcoholic solution, we obtain a residue consisting principally of glutine, and possessing a strong adhesive power, almost equal to that of the original glue employed.

Nevertheless it cannot be denied that Stelling's process has a certain value—very small, it is true—for the valuation of glues; above all when we have to deal with products of superior quality, products containing substances soluble in alcohol, in quantities much smaller than are present in ordinary glues.

Fels's method—that is, the determination of the viscosity—can also give very useful indications, but here again there are certain reservations which must be made. The viscosity is determined at 25° with an Engler viscosimeter. I claim to have discovered that solutions of glue undergo—after a more or less prolonged time of standing—modifications from the point of view of fluidity. In this way, a freshly prepared solution had a viscosity of 9·0°,

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but after standing for twenty-four hours it had assumed a gelatinous consistency. Another solution underwent the following modifications:—Its degree of viscosity was 3·7 after two hours, 4·8 after twenty-four hours, and 5·4 after forty-eight hours.

I would here recall that the process I described (*Chem. Zeit.*, 1893, xvii., 726), some years ago now, while being somewhat more complicated than the above, merits more confidence in judging the value of a glue. This process consisted in measuring the consistence of the jelly formed by 100 grms. of glue and 300 grms. of water.

The question of determining whether a given glue is good or bad, is one which is not easy to decide, unless we have to deal with a product that is altogether inferior. In the greater number of cases we simply endeavour to decide whether the glue is suitable for such and such a purpose.

As far as the adhesive power is concerned I have shown, by numerous experiments, that, from this special point of view, the glue from bones—which is of a decidedly inferior quality—is quite as good as that made from skin, which is of a superior quality. It is quite another matter in so far as the consistency of the jelly is concerned. The researches which I have carried out in this direction lead me to the conclusion that the jelly made from glues from skin is generally firmer than the jelly derived from glues from bone.

In the examination of a glue it must not be forgotten to notice the smell; this characteristic may give very useful indications as to the resistance of the product, and its tendency, or not, towards putrefaction; with regard to the above, skin glues are much better than those made from bone. Finally, the proportion of acid present in a glue is a matter of capital importance for certain purposes for which it is required. The method I have proposed (*Chem. Zeit.*, 1897, p. 691, and 1892, p. 1316) for the estimation of free and combined sulphurous acid, has once more enabled me to satisfy myself that glues from skin are superior to glues from bone. The determination of the water, ash, and fatty matters gives less important indications.—*Chemiker Zeitung*, 1898, p. 171.

THE ESTIMATION OF MANGANESE; ELECTROLYTIC SEPARATION OF MANGANESE AND IRON.

By F. KOEPPEL.

The author has devised a method enabling him at the same time to precipitate the manganese in the state of peroxide as a coherent powder, and to prevent the transformation of this peroxide into saline oxide by calcination in a platinum crucible. It is, of course, known that the platinum is strongly attacked in this operation.

The following is the method:—

The manganese salt is dissolved in 150 c.c. of water, and acetone is added. The solution is kept at a temperature of 50—55° C., and electrolysed with a current of 4 to 4·25 vols, and 0·7 to 1·2 ampères; care must be taken to add water to replace that which is gradually lost by evaporation. At the end of from two to five and a half hours, according to the proportion of acetone present (1·5 to 10 grms.), the operation is terminated; the peroxide of manganese is washed by means of a syphon, without interrupting the current; the electrode is dried at 150° to 180° C., and weighed.

The method for the electrolytic separation of manganese and iron, devised by the author, is sufficiently exact for commercial wants. In the presence of a great excess of pyrophosphate of soda, and a few drops of phosphoric acid, a solution of sulphate of iron and sulphate of manganese gives by electrolysis a deposit of metallic iron. A very small quantity of manganese is precipitated in the form either of binoxide or sesquioxide. The method is as follows:—

The solution of the mixed sulphates is poured, while stirring, into a boiling solution of 12 grms. of pyrophosphate of soda. When the solution has become perfectly clear we add 3 or 4 drops of phosphoric acid. If a slight cloudiness occurs, it suffices to add a slight excess of pyrophosphate of soda. The solution—which should be about 230 to 250 c.c. in volume, and have a decidedly alkaline reaction—is kept at a temperature of from 30° to 40° C., and electrolysed with a current of 1·8 to 2·5 ampères. The iron is completely precipitated in eight or nine hours. The deposit is washed with absolute alcohol, without interrupting the current, and the electrode is weighed after having been dried at a low temperature.—*Zeits. f. Anorg. Chem.*, xvi., p. 268.

SIXTH ANNUAL REPORT OF THE COMMITTEE ON ATOMIC WEIGHTS. RESULTS PUBLISHED DURING 1898.*

By F. W. CLARKE.

During the year 1898, there has been an increased activity in the determination of atomic weights, and a considerable number of investigations have been published. The importance of the subject is also indicated by the fact that the German Chemical Society has appointed a strong committee to report annually upon atomic weights; and its action for the current year is stated further on. The new data are as follows:—

Oxygen.

Keiser (*Am. Chem. Journ.*, xx., 733) has effected the complete synthesis of water by a new method, in which the hydrogen held by palladium, the oxygen, and the water produced are all determined by successive weighings in one and the same apparatus. For details of construction, &c., the original memoir must be consulted. The data for four experiments are as follows:—

Weight H.	Weight O.	Sum H+O.	Weight H_2O.
0·27549	2·18249	2·45798	2·45975
0·27936	2·21896	2·49832	2·49923
0·27091	2·15077	2·42168	2·42355
0·26845	2·13270	2·40115	2·40269

From columns first and second, the ratio H : O can be computed, while the first and fourth give the ratio H : H_2O.

Ratio H : O.	Ratio H : H_2O.
7·922	8·929
7·943	8·946
7·939	8·946
7·944	8·950
Mean .. 7·937	Mean .. 8·943

From ratio H : O .. .. O = 15·874
„ H : H_2O .. .. O = 15·886

Mean .. .. 15·880

This value is very near that obtained by Morley, 15·879; and has corroborative value. Its great merit is in the directness of the determination, and in the avoidance of complicated or troublesome corrections.

Nitrogen.

The equivalent of cyanogen has been determined by Dean (Chem. News, lxxviii., 261, November 25, 1898); but as yet only an abstract of his work has appeared. Silver cyanide was dissolved in nitric acid, and titrated

* *Journal of the American Chemical Society*, xxi., No. 2,

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by Stas's method with potassium bromide. The data give CN = 26·065; whence, if C = 12·01, N = 14·055.

Boron.

Armitage (Chem. News, lxxviii., 78: a paper read before the Chemical Society; not yet printed in full) has re-determined the atomic weight of boron by two methods. First, by determination of the percentage of water in borax, which had been washed with alcohol and ether successively, and then dried for six hours in a vacuum. The mean of six experiments gave—

B = 10·959.

Secondly, by the method of Rimbach. Fused borax was dissolved in water and titrated with dilute sulphuric acid. The mean of two experiments gave—

B = 10·928.

The abstract published gives no details of individual determinations, and neglects to state what values were assigned to the other atomic weights involved in the calculations, except that O = 16. The communication was discussed, in the main unfavourably, by Veley, Groves, Scott, and Dewar.

Armitage's paper called forth also a brief note from Leonard (Chem. News, lxxvii., 104), who refers to experiments of his own upon the dehydration of borax. He states that soda and boric acid are both volatilised when borax is intensely ignited, and that the composition of the residue is not constant. From this he concludes that the use of borax for determinations of atomic weight is liable to be attended by serious errors.

Zinc.

In the atomic weight determinations made some years ago by Morse and Burton, metallic zinc was converted into oxide, and in that way the ratio between metal and oxygen was measured. Later, Richards and Rogers showed that zinc oxide, prepared as Morse and Burton had prepared it, namely, by conversion of the metal into nitrate and subsequent ignition, always retained occluded gases, and in distinctly weighable quantities.

The research is now completed by the labours of Morse and Arbuckle (*Am. Chem. Journ.*, xx., 195, March, 1898), who have repeated the determinations made by Morse and Burton, with measurements of the occluded gases, and correction for them. In each experiment the gas, which consisted of oxygen and nitrogen, was analysed; and the corrections applied assume the litre weights to be, under standard conditions at latitude 45° and sea-level, 1·42923 grms. for oxygen and 1·25461 for nitrogen. The volumes are given in cubic centimetres.

Weight Zn.	Weight ZnO.	Volume gas.	Per cent O.	Atomic weight Zn.
1·19573	1·48860	0·468	26·28	65·459
1·03381	1·28707	0·402	18·14	65·445
1·06519	1·32599	0·342	18·42	65·459
1·05802	1·31711	0·312	18·58	65·440
1·26618	1·57619	0·521	13·82	65·489
1·03783	1·29198	0·408	35·28	65·475
1·08655	1·35276	0·412	19·55	65·437
1·11364	1·38647	0·456	18·62	65·447
			Mean..	65·457

O = 16. Vacuum weights are given. Without correction for occluded gases, Zn = 65·328, as against the earlier determination of Zn = 65·27. The new determinations agree closely with those of Richards and Rogers, who found Zn = 65·499, and of Richards alone, who found Zn = 65·404. The value assigned to zinc in the table of the Committee is 65·41, as published a year ago.

Cadmium.

In the case of cadmium the same uncertainty existed as in the case of zinc. Morse and Jones had determined the atomic weight by conversion of the metal into the oxide, in that way finding Cd = 112·06. Morse and Arbuckle (*Am. Chem. Journ.*, xx., 536, July, 1898) have repeated the investigation, this time with search for occluded gases in the oxide, and now give a new series of data, with corrections applied. In all essential features the research is parallel to that upon zinc, which had just been noted; and the results obtained are given in the subjoined table. The weights are reduced to a vacuum, and O = 16.

Weight Cd.	Weight CdO.	Volume of gas.	Per cent O.	Atomic weight Cd.
1·93188	2·20764	0·574	21·25	112·392
1·67935	1·91910	0·480	25·16	112·365
1·48430	1·69620	0·441	19·95	112·376
1·36486	1·55972	0·402	18·33	112·368
1·50295	1·71744	0·419	21·95	112·394
1·43804	1·64330	0·431	18·56	112·395
1·44041	1·64604	0·406	20·93	112·365
1·45938	1·66771	0·421	21·85	112·375
1·40379	1·60420	0·390	19·50	112·359
			Mean..	112·377

The uncorrected weighings give Cd = 112·084. Bucher, working with cadmium chloride and cadmium bromide, found the mean values 112·39 and 112·38, and the analysis of cadmium sulphate gave 112·36. These results accord fairly well with the determinations made by Dumas and by Huntington, but not with those of Hardin. The weight of evidence, however, now seems to be with the higher value, which may, with much probability, be adopted.

Cobalt and Nickel.

The paper by Winkler (*Zeit. Anorg. Chem.*, xvii., 236, June 25, 1898) upon these metals is merely a criticism of the determinations by Richards and Baxter and Richards and Cushman, which were noticed in the Committee Report for 1897. No new determinations are offered. Winkler suggests that the bromides prepared by Richards and his associates, which were sublimed in porcelain tubes, might have acted upon the glaze of the latter, and so have acquired impurities. He also suggests that perhaps the bromide might have retained an excess of hydrobromic acid, and he points out possible danger in the use of the Gooch crucible, in which the silver bromide was collected.

Selenium.

The atomic weight of selenium has been re-determined by Lenher (*Journ. Am. Chem. Soc.*, xx., 555, August, 1898), in the laboratory of the University of Pennsylvania. First, silver selenite was heated in a stream of gaseous hydrochloric acid, giving silver chloride, the latter being quite free from selenium. Three experiments gave as follows:—

Weight Ag_2SeO_3.	Weight AgCl.	Atomic weight Se.
0·98992	0·82715	79·326
1·59912	1·33600	79·373
2·70573	2·26087	79·320
	Mean	79·339

In a second series of eight experiments the silver chloride, after weighing, was reduced to metal in a stream of hydrogen. Thus the ratio between silver selenite and silver was measured. The weighings were as follows:—

Weight Ag_2SeO_3.	Weight AgCl.	Weight Ag.
0·26204	0·21897	0·16480
0·58078	0·48522	0·36534
0·70614	0·58999	0·44417
0·80811	0·67532	0·50821
0·98396	0·82232	0·61882
1·29685	1·08350	0·81562
1·63103	1·36288	1·02588
2·00162	1·67234	1·25884

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Hence, for the atomic weight of selenium we have—

$Ag_2SeO_3 : AgCl.$	$As_2SeO_3 : Ag.$
79·299	79·356
79·371	79·280
79·350	79·301
79·282	79·369
79·263	79·358
79·361	79·277
79·316	79·320
79·358	79·357
Mean .. 79·325	Mean .. 79·329

Still another set of determinations was based upon analyses of ammonium bromoselenate, Am_2SeBr_6. This salt was reduced by hydroxylamine hydrochloride, and the precipitated selenium was weighed in a Gooch crucible. The results are subjoined :—

Weight Am_2SeBr_6.	Weight Se.	Atomic weight Se.
1·00059	0·13324	79·243
1·50153	0·20022	79·367
2·00059	0·26649	79·273
2·00126	0·26657	79·269
3·00125	0·39958	79·226
4·00216	0·53346	79·333
5·00218	0·66656	79·306
5·03001	0·66998	79·267
Mean		79·285

General mean of all twenty-seven determinations—

Se = 79·314.

The antecedent values are O = 16, H = 1·008, N = 14·04, Ag = 107·92, Br = 79·95, Cl = 35·45. All weights were reduced to a vacuum.

The result obtained is near that found by Dumas, but considerably higher than that given by Ekman and Pettersson. The reason for this disaccordance is yet to be found. In the table at the end of this paper the value assigned to selenium is the mean of Lenher's determination, and the value given in the Report of last year, namely, when O = 16,—

Se = 79·17.

Neither the new nor the old determinations can be yet adopted to the exclusion of the other, and the mean value is the safest for present use.

Tellurium.

Metzner (*Ann. Chim. Phys.*, [7], xv., 272, October, 1898) has employed two methods for determining the atomic weight of this element. First, by synthesis of the sulphate, Te_2SO_7, which is perfectly stable at 440°. The tellurium which served as the starting-point was prepared by dissociation of hydrogen telluride, and was crystallised in beautiful needles. By solution in sulphuric acid, evaporation to dryness, and calcination at temperatures not over 440°, the sulphate was produced. The weights given are probably m.grms.

Weight Te.	Weight sulphate.	Atomic weight Te.
790·2	1235·0	127·9
414·3	647·5	128·0
1098·3	1717·0	127·8

Metzner's second method consisted in reducing tellurium dioxide by carbon monoxide in presence of metallic silver. The latter prevents the volatilisation of tellurium.

Weight TeO_2.	Loss of weight.	Atomic weight Te.
743·2	118·8	127·8
1106·7	221·3	128·0
988·5	197·0	128·24
1312·5	263·0	127·75

Metzner adopts 127·9 as the final result of his investigation. Apparently his weights were not reduced to a vacuum, and he neglects to state what value he assumed for the atomic weight of sulphur. O = 16 was evidently the basis of his calculations.

The work of Metzner called forth two theoretical papers by Wilde (*Comptes Rendus*, cxxvii., 613, 616), who holds that the experiments show that the true value for tellurium is 128. In his second paper he discusses the positions of tellurium and iodine in the periodic system. As both communications are purely critical in character, and contain no new data, they need no further notice here.

Still another set of determinations relative to tellurium is due to Heberlein ("Beitrage zur Kenntnis des Tellur's," Doctoral Dissertation, Strassburg, 1898). First, telluric acid was dissolved in hydrochloric acid, and the liberated chlorine was distilled off into a dilute solution of potassium iodide. In the latter iodine was set free, and was titrated with a decinormal solution of sodium thiosulphate. The values found for Te, with O = 16 and H = 1·008, are—

127·16
127·28
127·32
127·35
127·09
Mean .. 127·24

Secondly, telluric acid was transformed into tellurium dioxide, by heating with proper precautions to avoid loss.

Weight $H_2TeO_4.2H_2O$.	Loss of weight.	Atomic weight Te.
1·35236	0·41431	126·60
1·76859	0·54122	126·84
Mean		126·72

Thirdly, tellurium dioxide was reduced to tellurium by means of hydrogen in presence of metallic silver.

Weight TeO_2.	Loss of weight.	Atomic weight Te.
1·35908	0·37353	126·99
1·94038	0·39050	127·00
Mean		126·995

The mean of all three series is Te = 126·985.

It will be seen that some of these values range below, and others above, the atomic weight of iodine. Heberlein regards the higher figures as too high, and the lower as probably too low, the mean of all being most nearly correct. The main question, the position of tellurium in the periodic system, he considers experimentally unsettled, but favours the opinion that more critical determinations will place it below iodine and in the sulphur-selenium group. The value which he has actually found is only a trifle higher than that of iodine, and better determinations may well reduce it to the necessary amount.

Thorium.

Brauner's work upon the atomic weight of thorium (CHEM. NEWS, lxxvii., 160, April 7, 1898) has as yet appeared only in abstract. The determinations were made with the normal oxalate, in which thorium dioxide was estimated by heating, and the C_2O_3 was measured by titration with potassium permanganate. The values found for thorium with O = 16 were—

232·50	232·33
232·46	232·50
232·45	232·44
232·31	232·35

In mean, Th = 232·42.

Zirconium.

Venable (*Journ. Am. Chem. Soc.*, xx., 119, Feb., 1898), in order to determine the atomic weight of this element, has availed himself of the oxychloride, $ZrOCl_2.3H_2O$. This compound can be crystallised from strong hydro-

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chloric acid, and dried in a current of gaseous hydrochloric acid at 100—125° without loss of its water. When dissolved in water in a platinum crucible, evaporated to dryness, and strongly ignited, pure zirconia, free from chlorine, remains. The ratio $ZrOCl_2.3H_2O : ZrO_2$ is thus determined, and from it the atomic weight of the metal is calculable. The results of ten experiments are given by Venable as follows:—

Weight $ZrOCl_2.3H_2O$.	Weight of ZrO_2.	Ratio.
5·25762	2·78450	52·961
3·53994	1·87550	52·981
3·25036	1·72435	53·051
1·52245	0·80708	53·012
1·98802	1·58274	52·969
2·11371	1·11920	52·949
2·38139	1·26161	52·978
1·90285	1·00958	53·055
2·61847	1·38658	52·954
1·07347	0·56840	52·951
26·64828	14·11953	52·986

Hence if O = 16, H = 1·008, and Cl = 35·45, the atomic weight of zirconium becomes—

90·78 in mean,
91·12 maximum,
90·61 minimum.

As further results are promised, this investigation is to be regarded as a preliminary research rather than as a final determination.

Cerium.

Brauner's paper upon the compound nature of cerium (CHEM. NEWS, lxxvii., 160, April 7, 1898) has also only appeared in abstract. By a series of fractionations oxides were obtained giving atomic weights ranging from 140·25 down to 130·70. As the atomic weight decreases, the colour of the oxide changes from white to reddish-brown orange. Brauner infers that cerium is accompanied by another metal of atomic weight about 110. Yttrium was looked for in the lower fractions, but not found; nor were there any lines in the spark spectra other than those of cerium. The supposed new element, like gadolinium, may have no characteristic spectrum.

(To be continued).

ON THE SOLUBILITY OF ARGENTIC BROMIDE AND CHLORIDE IN SOLUTIONS OF SODIC THIOSULPHATE.

By THEODORE WILLIAM RICHARDS
and
HENRY BURNELL FABER.

In the course of a series of experiments having a practical end as their chief aim, several determinations of the solubility of argentic halides in solutions of sodic thiosulphate were made. Since the data concerning this reaction are none too plentiful, it seems worth while to record briefly our incomplete work upon the subject.

The method of procedure was extremely simple. Solutions of sodic thiosulphate of known strength, made by dissolving weighed amounts of pure re-crystallised material in water, were agitated for varying lengths of time in test-tubes at a fixed temperature with an excess of argentic salt. The bromide had been freed from chloride by long-continued digestion with potassic bromide, and both argentic halides had been carefully washed, dried, and powdered. At the end of the allotted times, the agitator was stopped, the heavy precipitates were allowed to settle, and two portions were taken from each perfectly clear supernatant liquid by means of an accurate 5·00 c.c. pipette. The silver in these portions was now precipitated by sulphuretted hydrogen and collected on a Gooch crucible. Subsequently, the mixed precipitate and asbestos were treated with nitric acid in excess, the nitrous fumes were expelled, and the silver in the mixture was determined by Volhard's method.

The agitator, based upon the apparatus of Noyes (*Zeit. Phys. Chem.*, ix., 606; also Schröder, *Ibid.*, xi., 454), consisted simply of a rotating rod with a number of flat strips of brass soldered at right-angles to its axis. The rubber stoppered test-tubes were strapped to the brass strips by means of rubber bands, and the whole was immersed in a large Ostwald thermostat. A portion of the water of the thermostat was drawn off when it was desired to remove the solutions, so that the mouths of the test-tubes might be uncovered, and of course the projecting mouths were carefully dried. A spring curtain-rod supporter, easily obtained in New England, formed a very convenient support for the rotating rod when soldered to the sides of the thermostat. The results with the second solution showed that four hours' agitation was enough to insure saturation. No claim of great accuracy is made for the figures—indeed, the variations among them show their crudity—but they more than sufficed for our purpose, and are trustworthy enough to form an adequate basis for the remarks which follow.

The Solubility of Argentic Bromide in Solutions of Sodic Thiosulphate.

Temperature = 35°.

	Cryst. sodic thiosulphate in litre. Grms.	Weight of silver found in 5·00 c.c. solution. Grm.	Time of agitation.	Weight of AgBr corresponding to each grm. of thiosulphate. Grm.	AgBr corresponding to $Na_2S_2O_3$ Molecule.
1.	100	0·110	4 hours	0·376	0·496
2.		0·108			
3.		0·106			
4.		0·109			
		0·108			
5.	200	0·228	4 hours	0·390	0·515
6.		0·224			
7.		0·225			
8.		0·225			
9.		0·226	16 hours		
10.		0·223			
11.		0·220			
12.		0·223			
		0·224			
13.	300	0·339	4 hours	0·397	0·524
14.		0·340			
15.		0·347			
16.		0·341			
17.		0·344			
18.		0·337			
19.		0·337			
		0·341			
20.	500	0·613	4 hours	0·427	0·564
21.		0·611			
22.		0·611			
23.		0·619			
		0·613			

It is thus evident that the quantity of argentic bromide increases more rapidly than the quantity of the thiosulphate. In this respect the behaviour of the bromide resembles that of the chloride, as observed by Stetefeldt ("The Lixiviation of Silver Ores," Crar and Gerlach, Freiberg, Saxony). Hence, simply judging from the solubility, one has a right to infer that the solubility concerns itself with the undissociated part of the sodic salt, for this

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is the part whose proportion increases when the concentration is increased.

The nature of the equilibrium is obviously so complex that the molecular ratios could not be expected to consist of simple whole numbers. Neither could the solubilities of the two halides be expected to conform to one another. In order to test this point, the solubility of argentic chloride in a solution of sodic thiosulphate containing 200 grms. of the crystallised salt to the litre was determined. Four parallel analyses of 5·00 c.c. of the solution saturated at 35° yielded respectively 0·344, 0·341, 0·342, and 0·341 grm. of silver, or on the average, 0·454 grm. of argentic chloride per grm. of sodic thiosulphate. (Russell found 0·400 and 0·485 by two different methods; the first was evidently not saturated, the second supersaturated; Stetefeldt, pp. 19, 20). Thus, the molecular ratio was in this case 1 : 0·78 instead of 1 : 0·52 as in the case of the bromide. The difference is undoubtedly due to the different solubilities of the argentic halides in water, which of course must be factors in the complex equilibrium.

It is well known that from these solutions two well-marked double salts (Herschel, *Edin. Phil. Journ.*, 1819, i., 26 and 398; also Lenz, *Liebig's Ann. Chem.*, 1841, xl., 94)—or, more probably, complex salts—may be obtained by crystallisation; but, of course, this fact does not show that these salts exist in the solution. As Barth (*Zeit. Phys. Chem.*, 1892, ix., 217) has pointed out, however, the inability of the solution to give the ordinary reactions of silver shows that a complex ion must be formed. More light might obviously be obtained from observations on the freezing- and boiling-points, as well as of electrolytic conductivities; indeed, Barth made an interesting beginning in this direction, and obtained evidence of the existence of a trivalent acid ion in the solution.

We proceeded in a somewhat different manner. Instead of studying the behaviour of the pure double salt, we observed the change in the freezing-point caused by the addition of argentic bromide to solutions of sodic thiosulphate. In one trial, the addition of 0·8 grm. of argentic bromide to 26 grms. of a 0·54 mole-solution* of sodic thiosulphate *raised* its freezing-point 0·08°, while in another trial the addition of 0·25 grm. of argentic bromide to 19 grms. of a 0·4 mole-solution raised its freezing-point 0·03°. Further additions in both cases produced no further rise, although much more argentic bromide dissolved; indeed, in the first case a slight fall was subsequently observed.

According to modern hypotheses, such a rise in the freezing-point can be produced only by the diminution of the number of active particles present. In the present case, the addition of another salt with different ions must, as usual, increase rather than diminish the dissociation of the sodic thiosulphate molecule; hence, it could have diminished the number of active particles only by causing some of the undissociated material to condense into a complex structure, in which the silver is combined. Thus, further evidence of the plausibility of Barth's conclusion as to the existence of a complex ion is afforded. The fact that upon the further addition of argentic bromide, no further rise is produced may be accounted for by the possible concomitant formation of another complex group, containing more silver—a reaction which might involve an increase in the number of active particles. The substances corresponding to these stages may well be the salts $Ag_2S_2O_3.2Na_2S_2O_3.2H_2O$ and $2Ag_2S_2O_3.2Na_2S_2O_3.2H_2O$, which are actually known in the solid state. The double formula is assigned to the second salt simply in order to show at a glance that it contains more silver than the first. It is more likely that this second salt possesses a simpler formula, and that its partial formation, even in the beginning, prevents the rise in the freezing-point from being as great as it would be if influenced by the formation of ions of the first salt alone.

In the course of the work, the depression of the freezing-point of water caused by the addition of sodic thiosulphate was also observed, as follows:—

Grm.-mol. in litre.	Depression of freezing-point.
0·202	0·855°
0·404	1·590°
0·535	1·980°

In brief, this paper contains data concerning the solubility of argentic bromide and chloride in solutions of sodic thiosulphate, cognate results upon the freezing-points of the solutions, and a few remarks upon the probable nature of the complex substances formed. The subject is one of great interest, but the time at our disposal, as well as the inherent obscurity of the equilibria of concentrated mixed solutions, does not suffice to present a more complete view of the details of the reaction.—*American Chemical Journal*, xxi., No. 1.

* That is, a solution containing 0·54 × 248·3 grms. of sodic thiosulphate in a litre. Such a solution would be called by some a 0·54 normal solution; but it seems to us that this nomenclature is an unfortunate one, and that the term "normal solution" should be reserved for the *equivalent* solutions so useful in volumetric analysis.

A REVISION OF THE ATOMIC WEIGHT OF COBALT.*

Second Paper.—The Determination of the Cobalt in Cobaltous Bromide.

By THEODORE WILLIAM RICHARDS and GREGORY PAUL BAXTER.

In a recent paper upon the atomic weight of cobalt (*Proc. Amer. Acad.*, xxxiii., p. 115) we began the analysis of cobaltous bromide by the determination of its bromine, with results which seemed to show that the atomic weight of cobalt is very nearly 58·99 (O = 16). Although very great care was taken in purifying the cobaltous bromide used in this work, it was never certain that during the sublimation of the bromide in the porcelain tubes small amounts of impurity had not crept in. The situation here was exactly the same as in the research upon nickel, carried on at the same time in this Laboratory (see *Proc. Amer. Acad.*, xxiv., p. 327; also Chem. News, vol. lxxix., p. 163), and here also the simplest and most convincing way of settling the question was to determine directly the amount of cobalt present in the salt, thus obtaining its total percentage composition.

Of the three methods of procedure which presented themselves—precipitation, electrolysis, and reduction of the bromide—reduction by hydrogen was chosen as being the least complicated and most certain. The slight hope offered in the nickel research that electrolysis might be used for the determination of the metal was here lacking on account of the greater difficulty in obtaining a satisfactory electrolytic deposit.

A conceivable objection to the use of the reduction of an *oxide* as an accurate quantitative method is the possibility that this reaction may not be capable of absolutely complete fulfilment. It is well known, for example, that one is rarely able to re-oxidise wholly a metal once reduced, even if the material is finely divided. In the case of the oxide there is no means of deciding whether or not the last traces of oxygen have been removed, while in the case of the *bromide* a residue of halogen is easily detected. The complete reduction of nickelous bromide described in the preceding paper shows that some such operations are in fact possible. It is easy to see how the increase in volume involved in oxidation might cause a part of the metal to be permanently protected by the growing coat of oxide; on the other hand, an oxide or salt which is being reduced leaves only its skeleton behind, the innermost

* Contributions from the Chemical Laboratory of Harvard College. From the *Proceedings of the American Academy of Arts and Sciences*, vol. xxxiv., No 14, February, 1899.

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meshes of which may be penetrated by the reducing agent.

Cobaltous bromide when heated in a current of dry hydrogen begins to be reduced at a temperature of about 350°. At higher temperatures the reduction goes on more rapidly, but is then accompanied by partial sublimation of the bromide. Schützenberger's (*Compt. Rend.*, cxiii., 177) observations on the sublimation of nickelous chloride were similar to these, but he seemed to think that some strange compound must have been the medium of the change, instead of realising that in the presence of hydrochloric acid a trace of the vapour of the metallic salt might easily exist even in an atmosphere of hydrogen.

If the hydrogen is *moist*, however, the action begins at a lower temperature, about 250°; but even under these conditions sublimation can be completely avoided only with the greatest difficulty. The reduction of *nickelous* bromide offered fewer difficulties: this process could be effected in a current of dry hydrogen, and without danger of sublimation of a trace of the material. The fact that moist hydrogen is more efficient than the dry gas is easily explained by the hypothesis that the oxide is formed as the first step in the reaction.

Purification of Materials.

Preparation of Cobaltous Bromide. — The cobaltous bromide used in this work was prepared by methods similar to those used in our previous investigation, and for details the previous paper should be consulted. Pure metallic cobalt was heated in a current of pure bromine and hydrobromic acid, and the sublimed bromide was preserved in weighing bottles contained in desiccators until used for analysis. Samples I. and II. were essentially the same as in the earlier investigation, even greater pains having been taken, however, in the purification of the reagents and water used in their preparation. Sample III. likewise was purified by essentially the same method as before, but was then further treated by six additional re-crystallisations as the purpureo-chloride, with the help of very pure re-distilled ammonia and hydrochloric acid. The oxides obtained from these preparations were finally reduced by means of pure hydrogen, instead of by ammonia as before.

Preparation of Bromine.—Here, also, the process of purification did not differ from that previously employed. The purity of the bromine is sufficiently proven by two analyses in which a known weight of silver was precipitated by a slight excess of ammonic bromide made from the halogen.

Ag in vacuum, Grms.	AgBr in vacuum. Grms.	AgBr : Ag.
2·91386	5·07226	57·447
2·97097	5·17170	57·447
	Average ..	57·447
	Stas found..	57·445

The balance and weights used in this work were the same as those described in our previous paper. The weights were carefully re-standardised, the values differing from those previously found by only a few hundredths of a milligrm. Since the balance was wholly free from iron, no inaccuracies could have arisen from magnetic attraction, either in this work or in that upon nickel.

Owing to the fact that the specific gravity of cobalt is almost identical with that of brass, no correction was required to reduce the weight of the cobalt to a vacuum standard.

The correction of +0·00010 grm. per grm. of cobaltous bromide was applied in each case to the weighings of that material. All weighings were made by substitution, as usual.

We are indebted to the Cyrus M. Warren Fund for Chemical Research, in Harvard University, for some of our more expensive pieces of apparatus.

Method of Analysis.

By means of the glass apparatus described in our earlier paper, cobaltous bromide, contained in a platinum boat, was dried in a current of pure dry nitrogen and hydrobromic acid gas in a hard glass tube heated to about 400°; and after the tube had been thoroughly swept out with nitrogen, and then by dry air, the boat was transferred to a weighing bottle in this safe atmosphere. The bottle was then weighed, and the boat carefully placed in the reduction tube, where it was heated in a current of moist hydrogen until the fumes of hydrobromic acid ceased to come off. The tube was then swept out with dry hydrogen, and when cool the boat was quickly replaced in the weighing bottle containing dry air, and was thus weighed after a suitable delay. In most analyses this process was repeated until the weight of the cobalt ceased to change. Cobalt reduced from the bromide is less constant in weight than nickel, gaining several tenths of a m.grm. in weight in twenty-four hours. For this reason the metal was always allowed to become thoroughly cool in the atmosphere of hydrogen, and the weighing bottle was allowed to come to perfect equilibrium with the atmospheric conditions inside a desiccator at the room temperature before receiving the boat. After half an hour *nickel* treated in the same way had been found to come to constant weight, and in half an hour the opportunity for oxidation of cobalt is so slight as to be negligible; hence this interval was the one which always elapsed between the bottling and the weighing of the cobalt. In one analysis, to see if exposure to the air affected the weight of the cobalt, the boat was bottled in dry nitrogen in the bottling apparatus, after being heated to constant weight in the usual way. Upon correcting the weight of the bottle for the difference in weight of nitrogen and air, the weights obtained by both methods agreed perfectly.

The resulting cobalt was in the form of a grey metallic sponge, which showed no traces of oxidation upon standing in air. Since previous work by other experimenters (Neumann and Streintz, *Monatshefte für Chem.*, xii., 642; *Berichte d. d. Ch. Gesell.*, xxv., 187 R; Hempel and Thiele, *Zeitschr. Anorg. Chem*, xi., 93) is not unanimous as to the occlusion of hydrogen by cobalt under these circumstances, it seemed desirable to us to obtain more evidence on this point. Accordingly, in several analyses the boat containing the cobalt was placed in a hard glass tube sealed at one end. After the air had been exhausted by means of a Sprengel pump, the tube was heated to about 500°, the highest temperature used in the reduction. In no case was a measurable quantity of gas evolved, and the cobalt did not lose in weight; hence it would appear that cobalt prepared from the bromide does not possess the property of occluding important amounts of hydrogen when heated in the gas.

To avoid any possibility of error, 2½ grms. of cobalt, freshly reduced from the bromide and allowed to cool in hydrogen, were subjected to quantitative combustion in the manner already described in the paper upon nickel. Only five-tenths of a m.grm. of water were formed; and even the repeated reduction and combustion of the residual oxide yielded only a m.grm. Evidently the amount of hydrogen occluded was very small. On the other hand, cobalt reduced originally from the oxide, when treated in the same way, was found to contain about fifteen times its volume of hydrogen, and when allowed to remain in hydrogen several hours it was found to have absorbed amounts comparable to those found by Neumann and Streintz (*loc. cit.*). A fuller statement of the experiments will be reserved for a future paper upon the nature and causes of these singular irregularities; for the present it is sufficient to have shown that cobalt, like nickel, reduced from the bromide, does not retain enough hydrogen to vitiate the results recorded below.

It is perhaps worth while to state also that the empty platinum boat was tested as to its power of absorbing weighable amounts of hydrogen. After ignition and

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cooling in the gas, and bottling in dry air as usual, it was found to have gained 0·02 m.grm. when compared with its weight after ignition in air. Evidently the occlusion of hydrogen, if measurable at all, is balanced by absorption of air; hence for our purpose it may be neglected.

A slight sublimation of the cobaltous bromide took place during the reduction in almost every case. The amount of this sublimed material was determined by washing out the tube with a few c.c. of nitric acid, and evaporating this liquid to dryness. After the solution of the residue in water and the addition of an excess of ammonia, a very dilute standard solution of potassic permanganate was run in until a pink colour appeared. This method of Winkler's is applicable only when extremely small amounts of cobalt are present, because the brown colour of the cobaltic salt interferes seriously with the end point in the presence of large amounts of cobalt. The weight of the cobaltous bromide thus sublimed never amounted to more than three-tenths of a m.grm., and seldom exceeded one-tenth of a m.grm.

The platinum boat used in the earlier work served to contain the bromide in these experiments also. Although the metallic cobalt alloyed itself with the surface of the boat to a slight extent, we were able to remove completely the alloy by treating the inside of the boat with aqua regia. After this treatment and scrubbing with round sand, the boat showed no trace of darkening upon ignition. Evidently, then, the cobalt had been completely removed. Of course a gradual loss of weight took place, owing to solution of small amounts of platinum, but this loss amounted to only half a grm. in the course of the work.

(To be continued).

THE HODGKINS MEDAL.

A few weeks ago we announced the award of this Medal to Professor Dewar. With much pleasure we print the following letter from Professor Langley, accompanying the Medal.

Smithsonian Institution, Washington,
April 3rd, 1899.

Dear Sir,

A Medal has been established under the name of the Hodgkins Medal of the Smithsonian Institution, which, in conformity with the will of its founder, is intended to be awarded only for exceptionally important contributions to our knowledge of the nature and properties of atmospheric air, or for practical applications of them to the welfare of mankind.

It gives me great pleasure to inform you, on the part of the Institution, that the first Gold Medal of the Hodgkins Foundation has been awarded to you in recognition of your indefatigable researches pursued for so many years, which have not only been potent in increasing and diffusing a more exact knowledge in regard to the nature and properties of air, but have opened the way for a practical utilisation of this knowledge in the advancement of human welfare.

I have now the honour to convey to you this Gold Medal accompanied by a duplicate impression in bronze, on behalf of the Smithsonian Institution, through the hands of the Ambassador of the United States in London, who, I am advised by the Department of State, is instructed to deliver it to you at the American Embassy in Victoria Street.

I beg to be allowed to add an expression of my gratification in being the medium by which this testimony of the Institution's admiration of your eminent services is conveyed, and of my personal regard.

I am, Sir, Yours with great respect,
(Signed) S. P. Langley,
Secretary.

Professor James Dewar, F.R.S.,
Royal Institution,
London, England.

NOTICES OF BOOKS.

Report of the Council of the Institute of Mines and Forests, on the present Gold and Forest Industries of British Guiana, for the Year ending June 30, 1898. Georgetown, Demerara: Baldwin and Co. 1898. Pp. 23.

The Council regret that they cannot report any marked progress in the industry; the amount of gold won has not fulfilled the hopes based on the large increase shown in the previous year, viz., 8911 ounces; it has, on the contrary, fallen below the production of 1895-96, and, in fact, is the lowest recorded for the last six years, viz., 117,265 ounces. This serious decrease is attributed to exceptionally bad weather, to the exhaustion of part of the alluvial workings, and to want of confidence arising from the unchecked dishonesty on the part of individuals entrusted with expeditions: this latter cause is, we are afraid, almost universal wherever there are gold-fields, and is to a large extent encouraged by the blind speculation on the part of the public, and the general ignorance of those responsible for the management and direction of the companies.

The amount of timber on which Royalty has been paid during this year is in excess of that for 1896-7, although the Customs returns are far less. This fact points either to the increase of local consumption or to large stocks being still on hand. The conservation of the valuable timber trees of the Colony is a matter the importance of which has been rather under-estimated in the past.

University College of Wales, Agricultural Department, Annual Report of Field Experiments. By J. A. Murray, B.Sc., and T. H. Middleton, B.Sc. Aberystwith: J. and J. Gibson. 1898. Pp. 42.

Two sets of experiments have been carried out; the first on manuring grass land, with the object of finding out which of the commoner sources of phosphates and nitrogen are the most suitable for the district, and what are the most economical proportions in which to apply them.

The area under experiment is a little over an acre, divided into thirty-five plots. The field was dressed in parallel lines, I. to VII., with different quantities of phosphatic manures, and cross dressed in lines A to E, with different quantities of the nitrogenous manures. At the end of four years the conclusions drawn were:—1. Nitrogenous manures should not be used alone; 2. Phosphate manures may be safely used alone; 3. Basic slag is better than superphosphate; 4. Nitrate of soda is better than sulphate of ammonia; and 5. The most profitable dressing is 3 cwts. of basic slag and 2 cwts. of nitrate of soda per acre. The whole of the results of this experiment, however, show that any one manure will exhaust the land if applied continuously by itself for a sufficiently long time.

Another experiment was to find the most profitable dressing of basic slag, but no definite results have yet been obtained.

Further experiments were made on the effects of sodium chloride and sulphate on plants other than mangels, from which it was found that common salt is injurious to grass, and that the injurious effect is due to the chlorine and not to the sodium.

Another series of experiments on meadow-hay show that on the whole nitrate of soda has decreased the crop, superphosphate of lime has increased it, kainit has largely increased it, lime—in the absence of potash and in conjunction with nitrate of soda—has decreased the yield of hay, and that a mixture of 4 cwts. of kainit and 4 cwts. of superphosphate has given a profit of 200 per cent. These conclusions are all based on the average of twelve years.

We are pleased to see that the University of Wales is doing such useful work, and only hope that the farmers will take advantage of and profit by it.

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Boron Food Preservatives, and their Influence on the Human Organism. London: Perkins, Bacon, and Co., Ltd. Pp. 63.

From the earliest times food has been preserved by means of salt, saltpetre, &c., but, as these bodies have only a slight antiseptic power, very large proportions had to be used; this has the effect of hardening and rendering meat less digestible, besides bringing on scurvy and scrofula. It has been found that boron possesses antiseptic properties far greater than that of salt or saltpetre, thereby rendering it possible to use a much smaller quantity. The new antiseptics have been largely used of late years, and among these one of the principal is boron.

The question has often been raised as to whether the continued use of boric acid was inimical to health; extracts from a large number of reports are here given to show that such is not the case. Fish, meat, butter, milk, bacon, &c., are all being preserved with borax, without impairing their nutritive qualities or having any deleterious effect on the health of the consumer. Of course a careful oversight must be exercised, and checks enforced as to the nature of the preservative used.

Borax appears to be the best of these antiseptics: it has no sour taste, and has no corrosive action on the skin; on the contrary, it is often used for allaying local inflammation. It possesses very slight physiological properties, is easily absorbed, and is quickly eliminated by the kidneys, whose secretions it promotes.

The results of a large number of experiments made by Dr. R. H. Chittenden, of Yale University, show that boracic acid and borax, when present in moderate quantities, have little or no deleterious effect upon the more important chemical processes of digestion; on the contrary, their presence may even accelerate the normal digestive processes of the alimentary tract.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

Note.—All degrees of temperature are Centigrade unless otherwise expressed.

Comptes Rendus Hebdomadaires des Séances, de l'Académie des Sciences. Vol. cxxviii., No. 14, April 4, 1899.

Reduction of Phosphate of Calcium by Carbon in the Electric Arc.—Albert Renault.—Referring to the recently published paper of M. Moissan on crystallised phosphide of calcium prepared in the electric furnace, the author announces that during his recent work on the reduction by carbon in the electric arc of the phosphorus acids, he obtained the phosphide P_2Ca_3. The most important property of this substance is its power of decomposing water and evolving the hydrogen in the form of phosphoretted hydrogen; this latter being entirely absorbed by copper sulphate, and not being spontaneously inflammable in the air. Under certain conditions, the details of which will be published later, the author obtained a mixture of calcium phosphides which gave with water both gaseous and liquid phosphoretted hydrogen at the same time.

Acetone Oils from the Dry Distillation of Pyrolignite of Lime as a Source of Methylpropyl Ketones.—A. and P. Buisine.—Pyrolignite of lime contains always, besides acetate of lime, of which the major part consists, small quantities of calcium salts of the highest volatile fatty acids. The crude acetone leaves, on its rectification, about 5 per cent of oil passing over above 70°. This product the authors call oil of acetone; from it has been extracted acetone, methylethyl ketone, methylpropyl ketone, methylbutyl ketone, and methylisopropyl ketone. To separate the latter oils from the mixture, the whole is shaken up with an excess of concentrated solution of bisulphite of sodium. The mixture becomes a pasty mass, from which the solid and liquid parts separate after standing for some hours. The liquid is separated by filtration at the pump, and the solid part washed with bisulphite solution and then with ether, and dried in the air. The bisulphide compound is decomposed by an excess of hot sodium carbonate solution. An oil separates, which is decanted off and dried over dry potassium carbonate. When distilled, this oil passes over almost entirely between 90° and 110°, and consists of a mixture of methylisopropyl ketone and methylpropyl ketone. These two can be separated from one another by repeated rectifications, the methylpropyl ketone forming by far the larger portion of the mixture.

Solanine.—P. Cazeneuve and P. Breteau.—There is a great difference of opinion about the composition and properties of solanine. The authors have investigated the matter afresh; their product gives on analysis the simple formula $C_{28}H_{47}NO_{10}.2H_2O$. It differs from the solanines hitherto described in the phenomena of its coloration products when in contact with strong sulphuric, nitric, and hydrochloric acid.

Berichte der Deutschen Chemischen Gesellschaft. Vol. xxxi., June 13, 1898.

Spectro-chemistry of Nitrogen.—J. W. Brühl.—The author has studied the optical properties of nitrogen and a series of its derivatives, principally:—(1) Nitrous and nitric acids, the nitrates, nitrites, and the nitro-carbides; (2) the hydrazines and the diazoïcs; (3) the oxynitro-derivatives; (4) the nitrosamines and the nitrosamides; (5) the nitramines and the nitramides; (6) protoxide of nitrogen, molecular nitrogen, and oxygen. His conclusions are that, in ammonia, hydroxylamine, the primary amines, and substituted hydrazines, nitrogen possesses the same atomic refraction. The atomic refraction of nitrogen is more feeble in the tertiary and secondary amides than in the corresponding amines. In binoxide of nitrogen, the refraction of the group NO is more feeble than in the nitrosamines and the alcoholic nitrites. The refraction of the group $\overset{N=N}{\diagdown R\diagup}$ is stronger than that of the ethylenic group. The nitramides, nitro-urethanes, &c., approach the groups N_2O_2 and NO_2. The nitrocarbides are comparable with the alcoholic nitrites. Nitrous acid in solution should have the formula $N(OH)_3$ or HO.NO; and nitric acid, its ethers and its salts, the formula RO—O—N=O.

Spontaneous Racemisation.—P. Walden.—Already noticed.

On Monobromacrolein and Tribromopropionic Aldehyde.—O. Piloty and A. Stock.—Non-polymerised bromacrolein is prepared by passing a vigorous current of steam through a solution of 30 grms. of acetate of soda in 80 c.c. of H_2O to which 100 grms. of dibromopropionic aldehyde has been added. The bromised aldehyde passes off with the first 100 c.c. Separate by decantation, dry over $CaCl_2$, and distil *in vacuo*. Bromacrylic aldehyde is a mobile colourless liquid, with a very pungent odour. Its formula is $CH_2=CBr—CHO$; it boils at 28·5° under 11 m.m., and at 111° under 420 m.m.; at normal pressure it boils at 120°, with partial decomposition; it is soluble in alcohol, ether, and warm water. It fixes bromine in the cold, forming tribromopropionic aldehyde, $CH_2Br.CBr_2.CHO$, boiling at 155° at the normal pressure, with decomposition; it is soluble in the organic solvents and in cold water.

The Tautomeric Forms of the α-Ketonic Ethers.—R. Schiff.—The chloralide of acetylpyruvic acid is obtained by heating acetyl-pyruvic ether with an excess of 3 mols. of anhydrous chloral to 100° in a closed vessel for three hours. The product is purified by crystallisation in benzene; it forms hard prisms fusible at 138°, soluble in alcohol, ether, warm water, and boiling benzene. The

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chloralide of benzoylpyruvic acid is prepared in a similar fashion, but by heating to 150°. The hard crystals, analogous to the others, are fusible at 198°.

Action of Benzylidene Aniline on the Ethers of the Non-saturated Oxy-acids.—R. Schiff and L. Gigly.—Acetonoxalic ether and benzylidene aniline unite molecule for molecule at the temperature of the water-bath, forming dihydrodiphenyldicetoacetylpyrrol; it crystallises in boiling amylic alcohol in needles which decompose at about 240°. Heated with hydroxylamine, it gives an oxime corresponding to the ketonic form, fusible at 215°. Pyruvic acid unites with benzylidene-aniline in acetic solution, forming dihydrodiphenyldicetopyrrol; it is a yellow powder, decomposing at 148°.

Action of Sodium on Dimethylacetylacetic Ether.—M. Conrad and R. Gast.—If we heat 86 grms. of dimethylacetylacetic ether to 110—120°, and gradually add 7 grms. of sodium, hydrogen is given off, and we obtain a white mass formed of a mixture of two soda derivatives. Supersaturate with dilute H_2SO_4, exhaust with ether, and distil. The portion coming over at 90—92° (24 grms.) is isobutyrate of methyl; the fraction passing at 228—232° (30 grms.) is γ-acetyldimethylacetylacetic ether (α-dimethyltriacetic ether). The soda derivative is a white crystalline mass, which does not react with the alcoholic iodides even when warm. The oxime crystallises in white needles fusible at 115°, and is soluble in alcohol; the dioxime has not been obtained. By heating with dilute hydrochloric acid or with baryta-water to 120° in a closed tube, we obtain acetylisobutyrylmethane, a yellowish liquid boiling at 171°.

Some Cases of Tautometry.—R. Schiff.—Ethylene-diacetylacetic ether is easily prepared by dissolving two molecules of acetylacetic ether and one molecule of acetic aldehyde in two volumes of alcohol and adding a little piperidine; leave in a cool place for twenty-four hours and precipitate with iced water. Isomerisation is produced when the ether is heated with alcohol. The enolic form is obtained in crystals when ethylene-diacetylacetic ether is dissolved in two molecules of ethylate of sodium, and neutralised exactly in the cold with dilute HCl. To separate the two modifications of ethylene-diacetylacetic ether we can make use of the combinations of this latter with the aromatic aldehydic bases.

On Diacetone-hydroxylamine, and on the Stereo-isomeric Aliphatic Ketoximes.—C. Harries and L. Jablonsky.—The authors have succeeded in isolating the two possible modifications of the oxime and the oxide of mesityl,—

$$(CH_3)_2.C{=}CH.C.CH_3 \quad \text{and} \quad (CH_3)_2.C{=}CH.C.CH_3$$
$$\qquad\qquad\quad \| \qquad\qquad\qquad\qquad\quad \|$$
$$\qquad\quad HO{-}N \qquad\qquad\qquad\qquad N{-}OH$$

On some Double Combinations of the Aromatic Ketones and Orthophosphoric Acid.—A. Klages and P. Allendorff.—Acetophenone unites directly with concentrated phosphoric acid, giving rise to the combination $C_6H_5.CO.CH_3+H_3PO_4$. It suffices to mix equimolecular quantities of the two substances. The ketone dissolves first, then the mass suddenly solidifies, with a considerable disengagement of heat; the product is then purified by crystallisation in ether. Phosphoric acid forms analogous combinations with other aromatic methyl ketones, and even with thienones. All these bodies are decomposed by water and by alcohol; they are equally decomposed if we attempt to distil them. Combinations of phosphoric acid with acetyl pseudocumene, and acetothienone are also described.

Action of Diazomethane on some Nitramines and on the Aromatic Nitro-derivatives.—J. L. Heinke.—Diazomethane reacts on the trinitro-derivatives, either by direct fixation or by giving rise to methyl-derivatives. Thus, with trinitrobenzene the reaction may be represented by the equation $C_6H_3N_3O_6+4CH_2N_2=C_{10}H_{11}N_5O_6+3N_2$. It acts on nitro-urethane in ethereal solution, giving nitrogen and methylnitramide.

MISCELLANEOUS.

Royal Institution. — On Tuesday next, May 2nd, Professor Silvanus P. Thompson, F.R.S., will deliver the first of a Course of Two Lectures at the Royal Institution, on "Electric Eddy Currents"; these are the Tyndall Lectures. On Thursday, May 4th, Mr. Lewis F. Day will begin a Course of Three Lectures, on "Embroidery"; and on Saturday, May 6th, Mr. W. L. Brown, L.R.C.P., will deliver the first of Two Lectures on "To Iceland in Search of Health." These lectures will be illustrated by the lantern. The Annual Meeting of the Members will be held on May 1st. The Friday Evening Discourse on May 5th will be delivered by Dr. W. J. Russell, F.R.S.: his subject is "Pictures produced on Photographic Plates in the Dark."

A New Method for the Estimation of Bismuth.—L. Vanino and E. Treubert.—If we heat, while stirring, a mixture of alkaline formaldehyd and a solution of a bismuth salt, the bismuth is completely precipitated in the metallic state. A slightly acid solution of the bismuth salt is mixed with the formaldehyd, and a large excess of a 10 per cent solution of caustic soda. The mixture is heated on the water-bath and continuously stirred, until the metallic bismuth is entirely deposited and the supernatant liquid becomes perfectly clear. We then add an excess of formaldehyd and caustic soda, and heat over a Bunsen for several minutes. The precipitate is washed by decantation with boiling water, then kneaded with a stirring-rod to bring it into a compact mass. It is collected on a tared filter or in a Gooch crucible, washed with absolute alcohol, and dried at 105° C. This reaction can be utilised for the separation of bismuth from certain other metals, such as aluminium, zinc, &c.—*Berichte*, xxxi. (9), p. 1303.

The Detection of Chromium in the presence of a Large Proportion of Iron.—A. Seyda.—The author has applied to this research a reaction which he seems to believe is new, but it was described nearly fifty years ago by A. Reynoso (*Ann. de Chim. et de Phys.*, 1851, [3], xxxiii., p. 324). The solution containing the mixture of the ferric and chromic salts is treated by an excess of an alkaline hydrate, then by permanganate of potash until the colour is persistent when warmed. After heating to about 100° for a quarter of an hour, the solution is cooled, and the excess of permanganate destroyed by means of a few drops of alcohol, and filtered. The chromium, transformed into an alkaline chromate, passes into the filtrate, which it colours yellow. If we desire any further characteristic of this compound, it is sufficient to acidulate with acetic acid, which will cause the pale yellow tint to change to an orange-yellow (dichromate); we then add one or two drops of plumbic solution; a bright yellow cloudiness is produced, due to the precipitation of plumbic chromate.—*Chem. Zeitung*, 1898, No. 22, p. 1085.

Merck's Digest.—Nos. 2 and 3.—These two numbers of this publication deal respectively with digitoxin and tropacocaine. Digitoxin is the most active glucoside contained in *Digitalis purpurea*. Its composition is represented by the formula $C_{28}H_{46}O_{10}$; it occurs as a white crystalline powder, soluble in alcohol and chloroform, slightly soluble in ether, and insoluble in water; it is stated that it possesses a quick, positive, and energetic action, and that untoward effects are seldom observed, and then only to a slight degree. The action manifests itself in from twelve to twenty-four hours; cyanosis and cardiac disturbances very often disappear by this time,—the pulse becomes strong and regular. It has also been found of advantage in pneumonia and typhoid. Tropa-

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cocaine or benzoyl pseudotropein was first obtained from Javanese coca leaves, and afterwards prepared synthetically from the tropine obtained by the decompositon of atropine and hyoscyamine. Its hydrochlorate has the formula $C_8H_{14}NO(C_7H_5O)$.-HCl, and occurs in colourless needles soluble in water and fusing at 271°. It is only half as toxic as cocaine, local stimulation is more rapidly produced and by less concentrated solutions, and recovery from its effects is more rapid. The action of tropacocaine on the nerve-centres is first stimulating, then paralysing from the brain down in decreasing degrees; but it prevents complete paralysis of the spinal cord or respiratory centres. Another advantage is that it keeps well in solution.

Carbonic Acid.—We understand that the Birmingham Oxygen Company are putting down in their works a large plant, of the most approved type, for the manufacture of pure carbonic acid gas under Steinem's and Murray's patents. Hitherto all supplies of this gas have been brought to the Midlands from London and Manchester, so that the plant must prove a valuable acquisition to the district.

MEETINGS FOR THE WEEK.

MONDAY, May 1st.—Society of Arts, 8. (Cantor Lectures). "Leather Manufacture." Prof H. R. Procter, F.I.C.
—— Royal Institution, 5. General Monthly Meeting.

TUESDAY, 2nd.—Royal Institution, 3. (The Tyndall Lectures). "Electric Eddy-currents," by Prof. Silvanus P. Thompson, D.Sc., F.R.S.

WEDNESDAY, 3rd.—Society of Arts, 8. "Ætheric Telegraphy," by W. H. Preece, C.B., F.R.S.
—— Society of Public Analysts, 8. "On some Comparative Analyses of, and Digestive Experiments with White and Whole-meal Breads," by O. Rosenheim, Ph.D., and P. Schidrowitz, Ph.D. "The Assay of Belladonna, B.P.," by F. C. J. Bird. "On the Use of Boric Acid and Formaldehyde as Milk Preservatives," by S. Rideal, D.Sc., and G. R. Foulerton, F.R.C.S. "The Value of the Estimation of Pentosans in Food Materials," by Otto Hehner and W. P. Skertchly.

THURSDAY, 4th.—Royal Institution, 3. "Embroidery," by Lewis F. Day.
—— Chemical, 8. "On the Combustion of Carbon Disulphide,' by H. B. Dixon and F. J. Russell. "The Action of Nitric Oxide on Nitrogen Peroxide," by H. B. Dixon and J. D. Peterkin. "On the Mode of Burning of Carbon," by H. B. Dixon. "Crystalline Glycollic Aldehyde," by H. J. H. Fenton and H. Jackson. "On the Blue Salt of Fehling's Solution and other Cuprotartrates," by O. Masson and B. D. Steele. "The Preparation of Acid Phenolic Salts of Dibasic Acids," by S. B. Schryver, D.Sc., Ph.D. "The Maximum Pressure of Naphthalene Vapour," by R. W. Allen, M.A.

FRIDAY, 5th.—Royal Institution, 9. "Pictures Produced on Photographic Plates in the Dark, by W. J. Russell, Ph.D., F.R.S.

SATURDAY, 6th.—Royal Institution, 3. "To Iceland in Search of Health" (with Lantern Illustrations), by W. L. Brown, L.R.C.P., L.R.C.S.

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THE CHEMICAL NEWS.

Vol. LXXIX., No. 2058.

THE ACETONE OILS AS DENATURALISING AGENTS.

By M. KLAR.

A great number of experiments have been made for the purpose of replacing wood-spirit and the pyridic bases by another denaturalising product offering more difficulties to the rectification of the denaturalised alcohol.

Dr. Lang, a Swiss chemist, has pointed out the conditions which a good denaturalising agent ought to fulfil; they are the following:—

1st, It should render the alcohol unfit for consumption.

2nd. It should not render alcohol more inflammable to any sensible extent, nor cause it when burning to give off toxic, fuliginous, or nauseous products.

3rd. The denaturalising material should be cheap and effective in small quantities.

4th. It should be easy to detect, and therefore not to be confounded with products normally present in alcohol of fermentation.

5th. Its chemical and physical properties should make the rectification of the alcohol so difficult that this operation cannot be carried on commercially with any advantage.

Dr. Lang thinks that the acetone oils answer these requirements; these oils are obtained as a by-product in the manufacture of acetone. The Swiss monopoly has bought 40,000 kilogrms. for a trial, and Dr. Lang has taken out a patent for the use of these oils as a denaturalising agent and for their preparation.

According to this patent, the portions distilled between 81° and 230° from commercial acetone comprise the higher homologues of acetone and of ethylmethylacetone, and can be utilised as denaturalising agents; in quantities of 1 per cent it makes the rectification of alcohol impossible, and in a much more certain manner than with the heavy benzenes used in France. If we take into account the low price of acetone oils,—about 36 francs per 100 kilogrms.,—and the small quantity shown by Dr. Lang to be sufficient, this method of denaturalising seems to possess great advantages; but we must also consider whether sufficient quantities of this substance (at present unused) can be manufactured, and if, with an increase in the demand, the output will be sufficiently great to prevent any rise in price.

Let us examine the possible sources of supply of the acetone oils. Dr. Lang quotes the following:—

1st. The higher acetones obtained as a by-product in the manufacture of methylacetone, by acetate of lime, from the distillation of wood.

2nd. The oils remaining after the rectification of raw wood-spirit.

3rd. The rectification of raw alcohols.

For this latter source M. Lang proposes a method of extraction which has never yet been carried out on the commercial scale,—that is to say, the oxidation of the fusel oils by means of a chromic mixture, the transformation of the volatile acids formed into salts of lime, such as the acetate, propionate, butyrate, and valerate, the desiccation of these salts and their dry distillation, which finally gives a mixture of ketones with a high boiling-point.

If we estimate the total annual consumption of denaturalised alcohol in Germany to be 50,000,000 litres, requiring 1 per cent of acetone oil, the quantity of oil necessary for its denaturalisation will be at least 500,000 litres. Let us see if the sources of supply proposed by Dr. Lang are able to furnish this quantity.

According to the most trustworthy sources of information there is produced in Germany 8,000,000 kilogrms. of acetate of lime, at the outside, to which must be added 9 000,000 kilogrms. of the same salt imported, or a total of 17,000,000 kilogrms. used for the production of acetone, and giving about 2 per cent of acetone oil, or about 350,000 kilogrms.; the rectification of 1,000,000 kilogrms. of raw acetone would give another 100,000 kilogrms. of acetone oil; there would therefore at present be a deficit of hardly 50,000 kilogrms. But it is in no way certain that the price would remain the same, and a syndicate might be formed.

As far as the acetone oils from the rectification of wood-spirit is concerned, the quantity may be put down at 200,000 kilogrms., but a part only of these oils could be used for denaturalising purposes.

As for the treatment of fusel oil, we ought not to rely upon it much, as it is in great demand; we find that in one year its price has risen from 25 to 55 per cent, and even at this price it is difficult to obtain as much fusel oil as is wanted. So this substance can hardly be looked upon as a source of supply.

M. Buisine has pointed out, as an important source of supply, the waste waters from wool washing; as a matter of fact a fermentation is set up in these waters which produces volatile fatty acids—acetic acid and capronic acid. It therefore suffices to distil this liquid in a current of steam, to obtain from 1 cubic metre of the water about 10 kilogrms. of acetic acid and 5 kilogrms. of propionic acid. As the towns of Roubaix and Tourcoing themselves give a daily supply of over 500 cubic metres of these wash waters, at least 12,500 kilogrms. of acetate of lime at 80 per cent, capable, according to M. Buisine, of giving a daily supply of 10,000 litres of acetone oils, can be obtained; but according to the author the return of oils would not be more than 3500 litres.

From the above data we are forced to the conclusion that Germany does not produce enough acetone oils to enable it to be used as the sole denaturalising agent, and that Lang's process for this country is of no practical interest. It would be otherwise if these oils were used as an alternative; for example, to replace wood-spirit for denaturalising in certain special cases; for instance, in 1895-96, 1,738,000 litres of alcohol at 100° were denaturalised with 5 per cent of wood-spirit; by replacing this with 1 per cent of acetone oil, only 17,000 kilogrms. of acetone oil, easy to procure economically, would have been required.

It has, further, been proposed to use, instead of wood-spirit, certain products therein contained, as a denaturalising agent. For instance, in 1881, Krämer and Lowenherz recommended allylic alcohol, which gave the desired result in proportions of 0·1 to 0·5 per cent in volume,—that is to say, ten or twenty times less than the acetone oil proposed by Dr. Lang. It certainly appears, however, from the above, that acetone oil cannot be considered as a substitute for wood-spirit.—*Zeit. f. Angew. Chemie*, 1898, p. 116.

Liquid Hydrogen.—At the Annual Meeting of the Members of the Royal Institution, held on May 1st, Professor Dewar made a brief reference to the recent scientific work of the Royal Institution, and announced that having obtained liquid hydrogen in considerable quantity he had directly determined its temperature and other physical constants, finding its boiling-point to be much lower than was previously supposed,—namely, 20 degrees above the zero of absolute temperature, and attaining by exhaustion a temperature of only 15 degrees absolute. Pending the discovery in quantity of some yet lighter gas, there was no means in sight of bridging this gap and reaching the zero point. He also took occasion to warn the public against absurd exaggerations as to the properties of liquid air, which, originating in America, found their way into popular magazines in this country.

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ON A NEW COLOURED REACTION OF THE BENZOYL RADICAL.

By G. DENIGÈS.

By using formolised sulphuric acid at 2 per cent (40 per cent commercial formol, 2 c.c.; concentrated sulphuric acid, 100 c.c.), a reagent I have already used for differentiating the polyphenols, I have found a very convenient test for the benzoyl radical $C_6H_5.CO$, which exists in a certain number of biological products and medicaments, such as hippuric and benzoic acids, cocaine, &c.

To obtain this reaction it suffices to introduce into a test-tube a small quantity of a benzolised substance, 2 or 3 c.c. of the formolised reagent, and a thermometer; heat gradually and carefully; if the substance under examination contains the benzoyl radical, we obtain, at about 120°, a brownish red colouration, showing a wide but rather diffused absorption band in the green part of the spectrum. The reaction is very marked, and can be produced with a very small quantity of the benzolised compound. I have obtained this colouration very easily with—

Benzoic acid	$C_6H_5.CO.OH$
Chloride of benzoyl ..	$C_6H_5.CO.Cl$
Benzoyl acetic anhydride	$C_6H_5.CO.C_2H_3O_2$
Benzol acetic acid	$C_6H_5.CO.C_2H_5O_3$
Benzamide	$C_6H_5.CO.NH_2$
Hippuric acid	$C_6H_5.CO.NH.C_2H_3O_2$
Cocaine or methyl benzoyl ecgonine..	$C_6H_5.CO.C_{10}H_{16}NO_3$.

The derivatives in which the benzoyl is connected direcly with the nitrogen, notably benzamide, require a rather longer contact at 120° than the other benzolised products, to give the desired colour.

The reagent used is coloured by other substances than the benzoyl derivatives, but the colouration in such cases generally shows itself at very different temperatures to 120°: this is the case with ordinary phenol; the polyphenols, the alkaloids of opium, &c., acting in the cold; and the salicylic products (salicylic acid, salicylamide). which decompose easily in warm phenol, in the presence of sulphuric acid, and colour this acid to which formol has been added, below 100°. Finally, the presence of the benzoyl radical may be hidden, if the nucleus to which it is fixed, or if the groups which surround it, are susceptible of reacting below 120° on the formolised sulphuric acid; such is the case with the ortho-forms and benzoic aldehyde.

With these reservations the coloured reaction just described may, if we observe the necessary precautions, be of great service for the identification of a considerable number of compounds used in pharmacy, or for the demonstration of the presence of the radical $C_6H_5.CO$, in certain natural or synthetic chemical bodies.—*Bull. de la Soc. de Pharm. de Bordeaux*, March, 1899.

SIXTH ANNUAL REPORT OF THE COMMITTEE ON ATOMIC WEIGHTS.

RESULTS PUBLISHED DURING 1898.*

By F. W. CLARKE.

(Concluded from p. 198).

The Didymiums.

JONES (*Am. Chem. Journ.*, xx., 345, May, 1898; CHEM. NEWS, lxxvii., 280) has determined the atomic weights of neodymium and praseodymium by means of the synthesis of the sulphates from the oxides. The material for the investigation was furnished by Waldron Shapleigh, and was very nearly pure. It was further purified by repeated fractional crystallisations of the double ammonium nitrates. From these salts the oxalates were prepared, and, from the latter, the oxides. The superoxide of praseodymium, Pr_4O_7, was reduced to Pr_2O_3 by ignition in hydrogen.

For praseodymium the results obtained were as follows, when O = 16 and S = 32·07:—

Weight Pr_2O_3.	Weight $Pr_2(SO_4)_3$.	Atomic weight Pr.
0·5250	0·9085	140·42
0·6436	1·1135	140·50
0·7967	1·3788	140·38
0·7522	1·3018	140·38
0·7788	1·3473	140·53
0·6458	1·1172	140·54
0·6972	1·2062	140·51
0·7204	1·2464	140·49
0·8665	1·4990	140·54
0·6717	1·1624	140·40
0·7439	1·2873	140·42
0·6487	1·1224	140·47
8·4905	14·6908	140·46

With O = 15·88, Pr = 139·41.

For neodymium the data are as follows:—

Weight Nd_2O_3.	Weight $Nd_2(SO_4)_3$.	Atomic weight Nd.
0·8910	1·5296	143·58
0·7880	1·3530	143·51
0·9034	1·5509	143·57
0·7668	1·3166	143·51
0·8908	1·5296	143·49
0·8848	1·5194	143·46
0·8681	1·4903	143·57
0·8216	1·4103	143·62
0·8531	1·4646	143·56
0·8711	1·4957	143·50
0·8932	1·5332	143·62
0·8893	1·5268	143·55
10·3212	17·7200	143·55

This value for neodymium must be corrected for the presence of a little praseodymium, which was estimated by the intensity of its lines in the spectrum. Corrected it becomes 143·6, or 142·52 when O = 15·88.

It is noteworthy that the values found by Jones almost absolutely reverse those given by von Welsbach, who puts praseodymium at 143·6 and neodymium at 140·8. Possibly the error in the latter figures may be only typographical.

Another determination of the atomic weight of praseodymium is due to C. von Schele (*Zeit. Anorg. Chem.*, xvii., 319), who worked up 100 kilos. of monazite to obtain his material for investigation. Two methods of determination were tried: one by synthesis of sulphate from oxide, the other based upon the oxalate. The oxide itself was prepared from the oxalate, and reduced from Pr_4O_7 —or, as von Schele gives it, PrO_2—to Pr_2O_3, by ignition in hydrogen. Disregarding a preliminary series of experiments made with impure material, and also the oxalate series, which gave unsatisfactory results, the final data are as follows:—

Weight Pr_2O_3.	Weight $Pr_2(SO_4)_3$.	Atomic weight Pr.
0·6872	1·1890	140·30
0·7834	1·3550	140·46
0·6510	1·1260	140·45
0·7640	1 3216	140·42
0·5183	0·8967	140·32
	Mean	140·40

This value, computed with O = 16 and S = 32, is sensibly identical with that found by Jones.

In the case of neodymium a single determination of

* *Journal of the American Chemical Society*, xxi., No 2.

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atomic weight has been published by Boudouard (*Comptes Rendus*, cxxvi., 900). 2·758 grms. of sulphate gave 1·605 of oxide, or 58·194 per cent. Hence, with O = 16 and S = 32, Nd = 143·045.

In this connection the spectroscopic work of Demarçay (*Comptes Rendus*, cxxvi., 1039), may also be properly noted. This chemist has studied the spectrum of neodymium obtained from diverse sources, and finds it to be definite and uniform. He therefore concludes that the metal is a distinct element, and not, as some chemists have thought, a mixture.

A preliminary notice, by Brauner (Chem. News, lxxvii., 161, April 7, 1898), of determinations of atomic weight upon the two metals in question, has also appeared. The material studied was obtained from Dr. Shapleigh, the determinations being made by the sulphate and oxalate methods. For praseodymium he obtained values ranging from 140·84 to 141·19, the average of thirteen determinations being Pr = 140·95.

Neodymium gave values from 143·4 to 143·63, but the material used still contained 2·5 per cent of praseodymium. Here, again, Welsbach's figures are reversed.

Miscellaneous Notes.

In a series of papers, Daniel Berthelot (*Compt. Rend.*, cxxvi., 954, 1030, 1415, and 1501) shows that the true molecular weights of gases can be computed from their normal densities with the help of their coefficients of compressibility. By suitable mathematical formulæ, from existing data, he computes the following values, taking O = 16 as his standard of comparison.

H	= 1·0074	
N	= 14·005	From N and N_2O.
C	= 12·005	From CO, CO_2, and C_2H_2.
A	= 39·882	
Cl	= 35·479	From HCl.
S	= 32·046	From SO_2.

From the density of nitrogen he finds N = 14·000; and from nitrous oxide, N = 14·007. These values he regards as superior to those determined by Stas, which are much higher; but Vézes (*Comptes Rendus*, cxxvi., 1714), in a critical note, expresses the contrary opinion. After all, a mathematical discussion of data depends for its ultimate value upon the accuracy of the data, and an exact theory applied to inexact material may yield inferior results. It may well be asked, therefore, whether the experimental data discussed by Berthelot are superior to those furnished by the researches of Stas—and this is the real point at issue. So far, the work of Stas does not seem to be overthrown.

The paper by Dulk (*Ber. d. Chem. Ges.*, xxxi., 1865, July 25, 1898), "Atomgewicht oder Atomgravitation," is essentially an abstract or summary of a book. Starting with H = 1, by a system of geometric configurations, the author computes a series of values for atomic weights, which are sometimes curiously near the experimental determinations. The following atomic weights are computed:—

Li	.. ..	7·0	B	.. ..	11·041
Na	.. ..	23·06	C	.. ..	11·9497
K	.. ..	39·111	Si	.. ..	28·0
Rb	.. ..	84·96	Cu	.. ..	63·339
Cs	.. ..	131·1	Ag	.. ..	107·717
Cl	.. ..	35·464	Au	.. ..	195·77
Br	.. ..	79·666	Hg	.. ..	198·45
I	.. ..	126·23	Zn	.. ..	65·385
N	.. ..	14·0	Cd	.. ..	112·0
O	.. ..	16·0	Tl	.. ..	204·298
F	.. ..	18·928			

New Tables.

Two new tables of atomic weights have appeared during the year; one by Richards (*Am. Chem. Journ.*, xx., 543, July, 1898), the other by a Committee of the

	Clarke. H = 1.	Clarke. O = 16.	Richards.	German.
Aluminum ..	26·91	27·11	27·1	27·1
Antimony ..	119·52	120·43	120·0	120·
Argon	?	?	39·9	40·
Arsenic	74·44	75·01	75·0	75·
Barium	136·39	137·43	137·43	137·4
Bismuth	206·54	208·11	208·0	208·5
Boron	10·86	10·95	10 95	11·
Bromine	79·34	79·95	79·955	79·96
Cadmium . ..	111·54	112·38	112·3	112·
Cæsium	131·89	132 89	132·9	133·
Calcium	39·76	40·07	40·0	40·
Carbon	11·91	12·00	12·001	12·00
Cerium	138·30	139·35	140·0	140·
Chlorine	35·18	35·45	35·455	35·45
Chromium ..	51·74	52·14	52·14	52·1
Cobalt	58·55	58·99	59·00	59·
Columbium ..	93·02	93·73	94·0	94·
Copper	63·12	63·60	63·60	63·6
Erbium	165·06	166·32	166·0	166·
Fluorine	18·91	19·06	19·05	19·
Gadolinium ..	155·57	156·76	156·0	—
Gallium	69·38	69·91	70·0	70·
Germanium ..	71·93	72·48	72·5	72·
Glucinum ..	9·01	9·08	9·1	9·1
Gold	195·74	197·23	197·3	197·2
Helium	?	?	4·0	4·
Hydrogen ..	1·000	1·008	1·0075	1·01
Indium	112·99	113·85	114·0	114·
Iodine	125·89	126·85	126·85	126·85
Iridium	191·66	193·12	193·0	193·
Iron	55·60	56·02	56·0	56·
Lanthanum ..	137·59	138·64	138·5	138·
Lead	205·36	206·92	206·92	206·9
Lithium	6·97	7·03	7·03	7·03
Magnesium ..	24·10	24·28	24·36	24·36
Manganese ..	54·57	54·99	55·02	55·
Mercury	198·49	200·00	200·0	200·3
Molybdenum ..	95·26	95·99	96·0	96·
Neodymium ..	142·52	143·60	143·6	144·
Nickel	58·24	58 69	58·70	58·7
Nitrogen	13·93	14·04	14·045	14·04
Osmium	189·55	190·99	190·8	191·
Oxygen	15·88	16·00	16·000	16·00
Palladium ..	105·56	106·36	106·5	106·
Phosphorus ..	30 79	31·02	31·0	31·
Platinum	193·41	194·89	195·2	194·8
Potassium ..	38·82	39·11	39·140	39·15
Praseodymium .	139·41	140·46	140·5	140·
Rhodium	102·23	103 01	103·0	103·0
Rubidium ..	84·78	85·43	85·44	85·4
Ruthenium ..	100·91	101·68	101·7	101·7
Samarium ..	149·13	150·26	150·0	150·
Scandium ..	43·78	44·12	44·0	44·1
Selenium	78·58	79·17	79·0	79·1
Silicon	28·18	28·40	28·4	28·4
Silver	107·11	107·92	107·93	107·93
Sodium	22·88	23·05	23·050	23·05
Strontium ..	86·95	87·61	87·68	87·6
Sulphur	31·83	32·07	32·065	32·06
Tantalum ..	181·45	182·84	183·0	183·
Tellurium ..	126·52	127·49	127·5	127·
Terbium	158·80	160·00	160·0	—
Thallium	202·61	204·15	204·15	204·1
Thorium	230·87	232·63	233·0	232·
Thulium	169·40	170·70	170·0	—
Tin	118·15	119·05	119·0	118·5
Titanium	47·79	48·15	48·16	48·1
Tungsten . ..	183·43	184·83	184·4	184·
Uranium	237·77	239·59	240·0	239·5
Vanadium ..	50·99	51·38	51·4	51·2
Ytterbium ..	171·88	173·19	173·0	173·
Yttrium	88·35	89·02	89·0	89·
Zinc	64·91	65·41	65 40	65·4
Zirconium ..	89·72	90·40	90·5	90·6

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German Chemical Society, consisting of Professors Landolt, Ostwald, and Seubert (*Berichte der Chem. Ges.*, xxxi., 2761, November 28, 1898). Both tables coincide in the main with that of your Committee, but in some instances there are differences which can be eliminated only by new investigations.

Richards's table is preceded by a careful discussion of some points at issue, especially as regards the atomic weights of antimony, cadmium, calcium, magnesium, platinum, tungsten, and uranium. For antimony, Richards prefers the value 119·92—or, in round numbers, 120—which depends on Cooke's analyses of the bromide, and involves the rejection of other data which seem entitled to some weight. For cadmium he accepts the higher value 112·3, rather than 112. Morse and Arbuckle's recent work lead me to adopt the value 112·38 for the present, bringing the Committee table into harmony with that of Richards. In the case of calcium, Richards regards the value 40·07 as too high, and adopts the round number 40. For magnesium, two values are in controversy, and here again Richards accepts the higher; in this case more evidence is needed. The same thing is true of platinum, tungsten, and uranium. The atomic weights of all three are uncertain to some tenths of a unit at least, and where Richards has selected data, I have preferred to use least square averages. New and better determinations are necessary in all three cases.

The Committee of the German Chemical Society present their table without discussion of the data, so that it represents their careful judgment as to the best values for analytical use, unencumbered by argument. All three of the members, however, argue at length in favour of O=16, as the basis of the scale, and give the well-known reasons in support of that view. Apart from theory, the oxygen scale certainly has the merit of greater convenience. The Committee also suggest the desirability of an international commission upon atomic weights, and in that all chemists are likely to agree.

In the accompanying table of atomic weight your Committee give first its own sets of values, based upon both standards, H=1 and O=16. These values are only rounded off to the second decimal place, and represent, so far, the actual results of re-calculation from the original data. Next is given Richards's table, and finally the table of the German Chemical Society, both sets of constants being more or less rounded off by the authors for convenience in practical use. It will be seen at once that the values adopted are in most cases sensibly identical. The new elements coronium, polonium, radium, monium, etherion, krypton, neon, xenon, and metargon are omitted, for lack of sufficiently precise data.

A REVISION OF THE ATOMIC WEIGHT OF COBALT.*

Second Paper.—The Determination of the Cobalt in Cobaltous Bromide.

By THEODORE WILLIAM RICHARDS
and
GREGORY PAUL BAXTER.

(Continued from p. 201).

In the first two determinations the hydrogen was generated from hydrochloric acid by means of pure zinc. It was purified by passing through bulbs containing silver nitrate, potash, silver nitrate again, then through a hard glass tube heated to redness. From this point the gas came in contact only with glass, being conducted through three towers containing glass beads moistened with silver nitrate, then by means of T-tubes, either directly in a moist state or through a long drying tube containing stick potash, into the reduction tube. The reduction tube was connected with the rest of the apparatus by means of a ground-glass joint.

A small amount of white sublimate, which appeared beyond the boat during each of the preliminary ignitions, proved to be ammonic bromide. The source of the ammonia was not at first apparent, as it was hard to believe that the cobaltous bromide could retain ammonic bromide at a temperature between 400° and 500°. Upon examination of the silver nitrate columns it was found that reduction had taken place there, metallic silver being precipitated upon the beads.

(The fact that silver nitrate is reduced by molecular hydrogen has already been noted by other experimenters: Russell, *Journ. Chem. Soc.*, 1874, [2], xii., 3; Pellet, *Compt. Rend.*, lxxviii., 1132).

Of course the reduction of the silver alone could do no harm; but unfortunately it was attended by a reduction of the nitric acid also. This was proved by passing the resulting gas through a hot tube, when traces of ammonia were formed, capable of easy detection by Nessler's reagent. We had come face to face with one of those frequent cases where an attempt at purification had introduced a flaw as serious as the one it eliminated. The very common use of argentic nitrate as a means of purifying hydrogen is obviously a pernicious one, if accurate results are desired.

The hydrogen apparatus was then entirely re-modelled. Owing to the fact that the amount of hydrogen required for the completion of a reduction was very much larger than the amount actually necessary to combine with the bromine (see the preceding paper, *Proc. Amer. Acad.*, xxiv., p. 333), a gasometer was constructed which should collect the hydrogen after it had passed through the tube and deliver it repeatedly to the apparatus, after removal of the hydrobromic acid. The hydrogen was generated by a primary battery consisting of zinc amalgam, hydrochloric acid, and platinised platinum. The gas delivered by this apparatus is pure, except for the presence of a little hydrochloric acid, which can be removed easily by means of potash. The accompanying cut shows the apparatus in its improved form.

The bottle B is filled with pure hydrogen generated by the battery C. From the bottle A water is syphoned into B, forcing the hydrogen by way of the stopcock *e* through the column D, filled with beads moistened with aqueous cupric sulphate to remove sulphur compounds taken from the rubber; through the columns E and F, which contain dilute sodic hydrate, then either directly through *g* or through a potash tube G into the reduction tube H. After being freed from hydrobromic acid in the bottle K containing potash, the gas is conducted through the open stopcock *b* into A. When B is full of water the process can be repeated by interchanging A and B, and opening the stopcocks *c* and *d* after closing *b* and *e*. The generator C served to keep the pressure always outward. The current of gas could be regulated by a pinchcock *a* on the rubber syphon tube. This apparatus proved entirely satisfactory, and was not altered during the investigation.

As in the case of nickel, it was found impossible by reduction alone to remove the last traces of bromine from the spongy cobalt. Even long-continued heating to a temperature much above the subliming-point of cobaltous bromide failed to give complete reduction, the solutions of the reduced cobalt giving decided tests for bromine. In the first analysis this bromine was precipitated with an excess of silver nitrate and weighed. In Analyses 2, 3, and 4 the cobalt was leached with pure water, and after filtration the bromine was determined in the filtrate. The solutions of the cobalt in dilute nitric acid proved almost entirely free from bromine, that obtained from Analysis 4 being entirely so. The silver bromide from these solutions was combined with that obtained from the aqueous extracts and weighed. As it was hard to believe that cobaltous bromide could be enclosed by the reduced

* Contributions from the Chemical Laboratory of Harvard College. From the *Proceedings of the American Academy of Arts and Sciences*, Vol. xxxiv., No 14, February, 1899.

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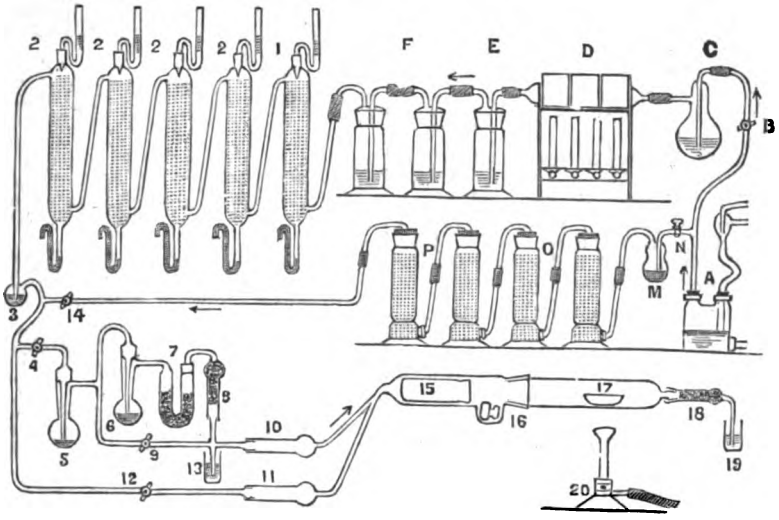

Fig. 1.—Apparatus for Igniting Cobaltous Bromide in any Desired Mixture of Gases.
The use of rubber was confined to the first part of this train, where it could do no harm (A B C D E F and A M N O P).

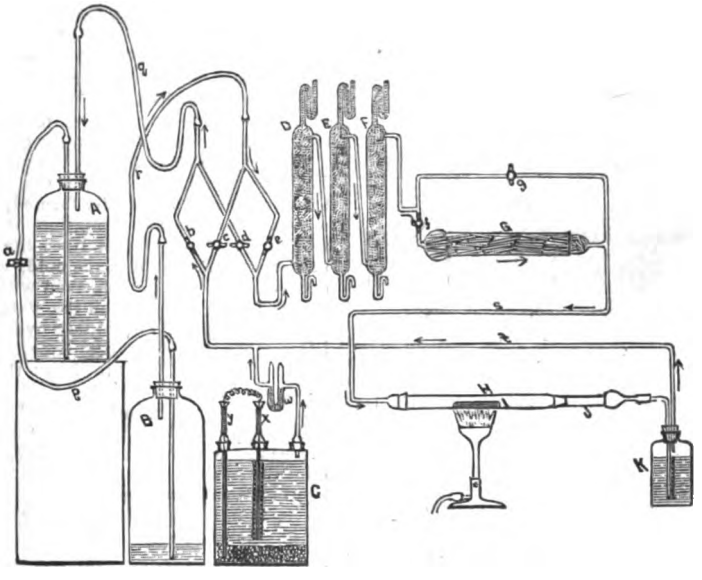

Fig. 2.—Apparatus for Reducing the Bromide.

cobalt in such a way as to remain unreduced and yet to go completely into solution with apparent ease, it was obvious that some foreign bromide must be present. Accordingly the filtrate from one of the precipitates of silver bromide was treated with an excess of hydrobromic acid, in order to remove the silver, and the re-filtered solution was evaporated to dryness. Upon a careful qualitative analysis tests were obtained for nothing but sodium and traces of cobalt. The sodium evidently came from the porcelain tube used in the sublimation, and we were dealing with an impurity precisely similar in source and nature to that described in the case of nickelous bromide. As the two investigations progressed side by side, the discovery was almost simultaneous in the two cases. We have already said that this outcome was not an unexpected one.

(To be continued).

PROCEEDINGS OF SOCIETIES.

CHEMICAL SOCIETY.

Ordinary Meeting, April 20th, 1899.

Professor Thorpe, F.R.S., President, in the Chair.

Messrs. A. J. While, W. J. Sell, and S. Godfrey Hall were formally admitted Fellows of the Society.

Certificates were read for the first time in favour of Messrs. Robert Henry Aders, 28, St. John's Wood Road. N.W.; Percy Bean, 42, Granville Road, Blackburn; Walter Lionel Blackman, Mostyn, Mount Nod Road, Streatham, S.W.; Wilfred Carpmael, 24, Southampton Buildings, Chancery Lane, W.C.; Frederick Doyle, 8,

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Woodlands Terrace, Middlesbrough; Frederick Charles Dunscombe, 54, Woodstock Road, Bristol; William Frederick Eichenauer, 58A, Maryon Road, Old Charlton, Kent; Friedrich Noel Ashcroft Fleischmann, Magdalen College, Oxford; Frederick Hutton Getman, 196, Atlantic Street, Stamford, Conn., U.S.A.; Julius Hübner, 24, Delanney's Road, Crumpsall, Manchester; Edward Charles Johnson, Lithgow, N.S.W., Australia; Arthur Alexander Leon, 13, Cleveland Square, Hyde Park, W.; James McAlley, Bankside, Falkirk; George Alfred Parkes, Muckomore Bleach Works, Co. Antrim, Ireland; Stanley John Peachey, 48, Grange Road, S.E.; Sidney Rossiter, 19, Ranelagh Road, West Green, N.; William Frederick John Shepheard, 12, Bridge Street Row, Chester; John Ward Stainer, 103, Cheriton Road, Folkestone; George Hardstaff West, Frankwell, Llanidloes.

The following Certificate was authorised by the Council under Bye-law I. (3):—

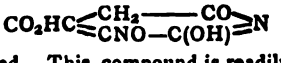
Bennetts, Benjamin Harvey, Gormanston, Mt. Lyell, Tasmania. Assayer. Two years' Student at the School of Mines, Ballarat, Victoria. At present Assayer for the Mount Lyell Mining and Railway Company, Tasmania.

Albert H. Turton. Harold Harris. *John Provis.*

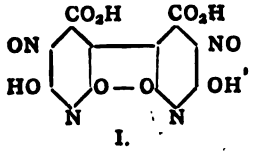
Of the following papers those marked * were read:—

* 48. "*The Synthesis of some ββ-Dipyridil Derivatives from Citrazinic Acid.*" By W. J. Sell, M.A., and H. Jackson, B.A., B.Sc.

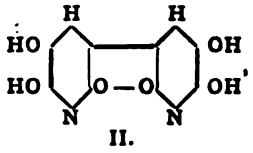
The present communication deals mainly with the constitution of some of the compounds described by Sell and Easterfield (*Trans.*, 1893, lxiii., 1035), of which little more than an analysis and brief description were given. It is now shown that citrazinic acid yields a nitroso-derivative, to which the formula—



may be assigned. This compound is readily oxidised by nitrous or nitric acids, producing the yellow acid represented by formula I.—



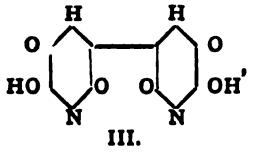
I.



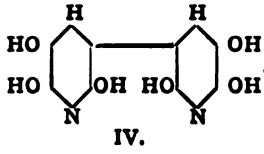
II.

Both these substances, on reduction, readily yield a very sparingly soluble compound having a bronze-like appearance, and possessing the constitution represeented by formula II.

The bronze-like substance reacts readily when boiled with fuming hydriodic acid and phosphorus, producing αα'-diglutaric acid, thus showing that these substances are derivatives of dipyridyl. With nitric acid it produces a golden-yellow, crystalline compound, to which the authors assign the constitution represented by formula III,—



III.



IV.

This substance is readily reduced to the bronze-like compound, and further reduction, either by hydriodic acid or stannous chloride, produces the hexhydroxy derivative having the constitution represented by formula IV.

If the bronze-like substance be heated at 100° with chlorosulphonic acid, a white, crystalline compound, having the formula $C_{10}H_4Cl_2O_3$, is produced.

*49. "*Action of Hydrogen Peroxide on Carbohydrates in the presence of Iron.*" By R. S. Morrell, M.A., Ph.D., and J. M. Crofts, B.A., B.Sc.

Cross and Bevan, in their paper on the reaction of carbohydrates with hydrogen peroxide (*Trans.*, 1898, lxxiii., 463), showed that substances which reacted with phenylhydrazine in the cold were formed. In September, 1898, some results of the reaction were communicated to the British Association, in which it was shown that the first product was undoubtedly glucoson. The glucoson had not then been isolated, but was identified by means of the osazone formed by the action of phenylhydrazine *in the cold*, and by the isolation of the methyl phenyl glucosazone, precipitated also in the cold. The formation of this methyl phenyl glucosazone was considered by Fischer to be one of the characteristic tests for the presence of glucoson.

The action of hydrogen peroxide in the presence of ferrous salts has been extended to levulose and galactose, to the pentose arabinose, and to the methyl pentose, rhamnose. Of these, levulose and arabinose have yielded results which are similar to those obtained with glucose, namely, the formation of an oson.

The oson was detected, in the case of glucose, by the formation, in each instance in the cold, of phenyl glucosazone (m. p. 205°), and of methyl phenyl glucosazone (m. p. 152°), both the glucosazones being analysed. The solution of the glucoson reduces Fehling's solution in the cold, and more strongly so on slightly warming. It yields precipitates in the cold with diamines, with hydrazine, and with substituted hydrazines.

It might be that the osazones were formed from the glucose directly, and not from the oson; the solution, however, after fermentation at 30°, was still found to react quite as readily with hydrazines in the cold. A small quantity of the oson isolated was found to have properties like those ascribed by Fischer to glucoson.

The behaviour of levulose is almost identical with that of glucose under like conditions of treatment. The oson formed is glucoson, and its identification rests on the same evidence as that given for glucoson from glucose.

With regard to arabinose, the action is again similar to that which takes place in the case of the hexoses. Arabinoson is undoubtedly formed, and its identification is established by the formation of arabinosazone in the cold, and more completely by the formation of methyl phenyl arabinosazone in the cold, whereas arabinose and methyl phenyl hydrazine, even with excess of the hydrazine and after warming on the water-bath, were found to form methyl phenyl arabinose hydrazone.

Galactose and rhamnose, under like conditions of treatment, also form substances of the nature of an oson, which are being investigated.

The action of bromine at 40° on the solution of the glucoson gives a liquid still strongly reducing, which reacts easily with phenyl-hydrazine, and forms, in the case of levulose, a soluble calcium salt of a dibasic acid, which is probably an oxysaccharic acid.

The course of the reactions may, perhaps, be expressed by the following equations:

$$\underset{\text{Glucose.}}{CHO\cdot CHOH\cdot(CHOH)_3\cdot CH_2OH} + O = \underset{\text{Glucoson.}}{CHO\cdot CO\cdot(CHOH)_3\cdot CH_2OH} + H_2O.$$

$$\underset{\text{Levulose.}}{CH_2OH\cdot CO\cdot(CHOH)_3\cdot CH_2OH} + O = \underset{\text{Glucoson.}}{CHO\cdot CO\cdot(CHOH)_3\cdot CH_2OH} + H_2O.$$

$$\underset{\text{Arabinose.}}{CHO\cdot CHOH\cdot(CHOH)_2\cdot CH_2OH} + O = \underset{\text{Arabinoson.}}{CHO\cdot CO\cdot(CHOH)_2\cdot CH_2OH} + H_2O.$$

Discussion.

Mr. Fenton said that he was very glad that Dr. Morrell had succeeded in bringing his observations on carbohydrates to the present stage. His results now nearly completed the series of investigations which had been

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undertaken with a view of studying the behaviour of typical hydroxy-compounds towards oxidising agents in presence of iron.

*50. "*The Condensation of Oxalic Acid and Resorcinol.*" By John Theodore Hewitt and Arthur Ernest Pitt.

The condensation of oxalic acid and resorcinol, on heating with concentrated sulphuric acid, has been studied by von Baeyer (*Ber.*, 1871, iv., 662) and Gukassianz (*Ber.*, 1878, xi., 1184). The former stated that the product obtained closely resembled euxanthone, the latter that two isomeric substances were formed, both having the formula $C_{14}H_8O_5$, but whilst one was soluble in alcohol and gave non-fluorescent alkaline solutions, the other was insoluble in alcohol, but dissolved in alkalis with a fine moss-green fluorescence.

The authors have studied the former of these two products, which is the chief product of the reaction. It is distinct from the substances obtained by Claus and Andreæ (*Ber.*, 1877, x., 1305; 1881, xiv., 2563) and von Georgievics (*Mitt. Technol. Gewerb-Mus. Wien*, 1898 [ii.], viii., 364). These chemists used an excess of oxalic acid as a condensing agent, and employed a higher temperature. Gukassianz misinterpeted the results obtained on combustion; his compound really has the formula $C_{20}H_{14}O_7$, and is probably a carboxylic acid. In addition to further analyses of this compound, the authors describe the following derivatives:—

Sodium and lead salts, $C_{20}H_{13}O_7Na$, $(C_{20}H_{13}O_7)_2Pb$. Triacetylated lactone, $C_{20}H_9O_6(C_2H_3O)_3$. Triacetylated acid, $C_{20}H_{11}O_7(C_2H_3O)_3$. Tetracetylated lactone of leuko-acid, $C_{20}H_{10}O_6(C_2H_3O)_4$. Product obtained from acid and benzoyl chloride, (?) $C_{14}H_7O_5(C_6H_5CO)$. Dinitro-lactone, $C_{20}H_{10}(NO_2)_2O_6$. Sodium salt of dinitro-acid, $C_{20}H_{11}(NO_2)_2O_7Na$. Triacetylated dinitro-lactone, $C_{20}H_7(NO_2)_2O_6(C_2H_3O)_3$. Tetrabrominated acid, $C_{20}H_{10}Br_4O_7$.

From the composition of the compounds described, the authors consider that the acid must be represented by the formula $[C_{18}H_9(:O)(OH)_4]:C\cdot CO_2H$.

51. "*Ethyl Ammonium Sulphite.*" By Edward Divers and Masataka Ogawa.

Dissolved in alcohol, sulphur dioxide and ammonia combine with each other and the alcohol to form a new salt, ethyl ammonium sulphite, which is a crystalline solid, subliming undecomposed in dry air, soluble in alcohol, insoluble in ether, and at once changed by water into alcohol and ammonium pyrosulphite. Hence, in preparing the salt, the absence of water must be carefully secured. Ethyl ammonium sulphite belongs to the series of new sulphites, or metal-sulphonates discovered within the last few years:—Phenyl sodium sulphite (Schall, 1892); methyl magnesium sulphite (Szarvasy, 1897); methyl and ethyl sodiumsulphites and ethyl potassiumsulphite (Rosenheim and Liebknecht, 1898), which are distinguished from alkylsulphonates in at once decomposing with water into phenol or alcohol and pyrosulphite, and in being formed by the union of sulphur dioxide with metal alkoxide or ammonium alkoxide. Warlitz's potassium ethyl sulphite has been shown by Rosenheim and Liebknecht to be only potassium ethylsulphonate. The new salts are not decomposed by excess of sulphur dioxide; Rosenheim and Liebknecht, who found that they were, must have allowed moisture to enter their vessels.

52. "*Ethyl Ammonium Selenite and Non-existence of Amidoselenites (Selenosamates).*" By Edward Divers and Seihachi Hada.

Selenium dioxide and ammonia, dissolved together in well-cooled alcohol, in the absence of any water, form a new salt, ethyl ammonium selenite, soluble in alcohol, insoluble in ether, and at once decomposed by water into acid ammonium selenite and alcohol. The salt soon begins to decompose at the common temperature, selenium being one of the products. Hinsberg obtained, in 1890, what appears to have been ethyl hydrogen selenite and ethyl phenyl ammonium selenite.

When water is also present, the ammonia and selenium dioxide do not unite with the alcohol, but with the water to form the ammonium selenites, a fact known to Berzelius. Cameron and Macallan (1888), proceeding apparently in the way the authors have prepared ethyl ammonium selenite, obtained instead salts which they describe as being selenosamates, But Cameron and Macallan record no property of their selenosamates which can serve to distinguish them from the half-acid and three-fourths-acid ammonium selenites, except their chemical composition, which was determined by methods of doubtful accuracy. The authors, therefore, believe that Cameron and Macallan cannot have taken sufficient precautions to exclude all moisture in their experiments, and conclude that there is no reliable evidence for the existence of amidoselenites. Accordingly, selenious acid seems to form no compounds analogous to amido-, imido-, or nitrilo-sulphates, any more than it forms salts like alkylsulphonates or salts having the constitution of metal sulphites.

Incidentally the authors obtained, in the pure state, normal ammonium selenite, half-acid ammonium selenite, and three-fourths-acid ammonium selenite.

53. "*The Allotropic Modifications of Phosphorus.*" By D. L. Chapman, B.A.

From experiments performed by the author, the following conclusions have been drawn:—

(1). "Metallic" and red phosphorus are identical. This is proved by their similarity in appearance when viewed under the microscope. The alleged higher vapour tension of some varieties of red phosphorus is due to impurity, which on heating decomposes with formation of phosphorus vapour.

(2). The vapours of red and ordinary phosphorus are identical. The vapour density of ordinary phosphorus has been determined at the boiling-points of mercury and of sulphur, and agrees closely with the density calculated on the assumption that the molecule consists of four atoms, although the results obtained by Mitscherlich and by Deville and Troost at higher temperatures would scarcely lead one to suspect that this would be the case.

(3). Red phosphorus melts, forming ordinary phosphorus, under pressure at the melting-point of potassium iodide. This point on the pressure temperature diagram the author proposes to call the triple point of red phosphorus. Melted ordinary phosphorus thus becomes superfused red phosphorus, and superfused ordinary phosphorus becomes the superfused liquid of both varieties. At ordinary temperatures red phosphorus is stable and white phosphorus unstable. Phosphorus, therefore, appears to possess in a remarkable degree the property of remaining in an unstable condition.

54. "*On the Interaction of Mercurous and Mercuric Nitrites with the Nitrites of Silver and Sodium.*" By P. C. Ray, D.Sc.

(1). *Mercuric and sodium nitrites.* To the neutral solution of mercurous and mercuric nitrites, the products of the dissociation of mercurous nitrite (*Trans.*, 1897, lxxi., 340), sodium chloride is added to remove mercurous salts. The filtrate containing mercuric and sodium nitrites, and possibly a small quantity of sodium chloride, is allowed to evaporate spontaneously. In course of time, an orange-red crystalline deposit is formed, followed by iodine-like scales, and finally crystals of sodium nitrate. Sometimes sodium nitrate is the only substance obtained. Unless sodium chloride is present, the coloured compounds are not formed. Analysis seems to show that the formula of the coloured substances is $HgCl_2.2HgO.\frac{1}{2}H_2O$, but they lose no weight in a desiccator over sulphuric acid nor when kept at 100°, but if heated in a bulb tube a deposit of moisture is invariably noticed. Millon, Thummel, Volhard, and Haack have described very similar compounds with the formula $HgCl_2.2HgO$, but no mention is made of any hydrated modification.

(2). *Mercurous and silver nitrites.* To a hot solution of

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mercurous nitrite (containing mercuric nitrite) solution of silver nitrite was added. There was no effervescence, but the liquid at once became cloudy, and was allowed to stand overnight. Next day a clear solution was obtained, having at the bottom a layer of dirty grey mercury, and above it a deposit of shining, minute crystals of silver.

Careful analyses showed that, not only was there no loss of nitrogen during the reaction, but that it remained entirely in the form of nitrite.

With dilute solutions no silver was precipitated. In the reaction between mercurous and sodium nitrites, the nitrogen remained as nitrite, the mercurous nitrite decomposing entirely into mercuric nitrite and mercury.

The true explanation of the reactions has yet to be found, and with this end in view the author intends to make further experiments with solutions of the nitrites in varying degrees of dilution.

(To be continued).

SOIRÉE OF THE ROYAL SOCIETY.

Wednesday, May 3, 1899.

List of Objects Exhibited by Sir William Crookes, F.R.S., illustrating his Photographic Researches on Phosphorescent Spectra.

It has long been known that certain substances enclosed in a vacuous glass bulb phosphoresce brightly when submitted to molecular bombardment from the negative pole of an induction coil. The ruby, emerald, diamond, alumina, yttria, samaria, and a large class of earthy oxides and sulphides, emit light under these circumstances. Examined in a spectroscope the light from some of these bodies gives an almost continuous spectrum, while that from others, such as alumina, yttria, and samaria, gives spectra of more or less sharp bands and lines. Since 1879 the author has been working on these phosphorescent spectra, chiefly in connection with the earths of the yttria group, and by chemical fractionation he has succeeded in separating from this group bodies whose phosphorescent spectra consist chiefly of single groups of lines, other groups being absent. For the last six years the research has been extended beyond the visible spectrum, and photographs of the ultra-violet portion of the spectra are now being taken with a spectrograph with a complete quartz train. Some of the results of this research are here exhibited.

A. Spectrograph with two quartz prisms, quartz lenses, and condensers for photographing the ultra-violet spectrum. The slit is of quartz, cut and polished according to the author's method described in the Chemical News, vol. lxxi., p. 175, April 11, 1895.

The prisms are made in two halves according to Cornu's plan; one half of each being right-handed and the other half left-handed. One of the lenses is also right-handed and the other left-handed. By this device the effect of double refraction is so completely neutralised that with a five-prism instrument it is impossible, under high magnifying power, to detect any duplication of the lines, although the resulting photographs of spectra can be measured to 0·01 $\mu\mu$.

The sensitive surface must be curved (Chemical News, vol. lxxii., p. 87, August 23, 1895; and vol. lxxiv., p. 259, November 27, 1896) and set at an angle to obtain good definition over the whole spectrum. In the present instrument, using the middle position showing the whole spectrum on a plate, the angle is 40°, and the curvature is 190 m.m. radius.

B. A diagram of the spectrograph to full size, showing the arrangement of prisms, lenses, and condenser, the curvature and angle of sensitive surface, together with the path of the rays. Celluloid films are used, glass not being sufficiently flexible.

C, Photographed spectra of an alloy composed of equal molecular weights of zinc, cadmium, tin, and mercury. This alloy has been chosen as giving a standard spectrum, the lines of which are accurately determined and sufficiently close together to leave no wide unoccupied gaps in the spectrum.

When photographing a metallic, gaseous, or phosphorescent spectrum the spectrum of this alloy is photographed on the same plate, the known lines partially overlapping the unknown lines, to facilitate the calculation of their wave-lengths.

D. Photographs of a group of lines high up in the ultra-violet region, characteristic of a new element associated with yttrium, and separated by long fractionation. To this element the name Victorium has been given.

E. Enlarged spectrum of the Victorium group of lines.

Victoria is an earth characterised by a group of lines in the neighbourhood of λ3110. In chemical characters it differs from yttria in many respects. From a hot nitric acid solution Victorium oxalate precipitates before yttrium oxalate and after terbium oxalate. On fractional precipitation with potassium sulphate the double sulphate of Victorium and potassium is found to be less soluble than the corresponding yttrium salt, and more soluble than the double sulphates of potassium with the terbium and cerium groups. Victorium nitrate is a little more easily decomposed by heat than yttrium nitrate, but the difference is not sufficient to make this reaction a good means of separating Victorium and yttrium. Fusing the nitrates can, however, be employed advantageously to separate mixed Victoria and yttria from the bulk of their associated earths. Tested by its position in a series of earths obtained by fractional precipitation with dilute ammonia, Victoria is found to be less basic than yttria and more basic than most of the earths of the terbia group.

The atomic weight of Victorium is probably near 117. In the purest state in which it has yet been prepared Victoria is of a pale brown colour.

F. Diagram of the fractionation of the crude yttria earths, showing the pedigree of Victorium.

PHYSICAL SOCIETY.

Ordinary Meeting, April 21st, 1899.

Mr. T. H. Blakesley, Vice-President, in the Chair.

A mathematical paper on "*The Effect of a Solid Conducting Sphere in a Variable Magnetic Field on the Magnetic Induction at a Point outside*," was read by Mr. C. S. Whitehead.

It is an investigation of the magnetic induction at a point outside a solid conducting sphere when magnetic disturbances are taking place in the dielectric envelope. An expression is given for the maximum value of the magnetic induction when the sphere becomes an infinite plate and the inducing system consists of an alternating current in a circular circuit whose plane is parallel to the plate, *i. e.*, when the maximum value of the induction tangential to the surface is zero. A second expression gives the maximum value of the magnetic induction normal to the surface for a point at considerable distance from the axis, and just outside the plate. In this latter case, the maximum value of the induction tangential to the surface appears as a function of the maximum current of known frequency in the inducing circuit, the various dimensions in space of the system, and the permeability and specific resistance of the plate. From these equations, taking the most authentic values of the involved constants, the maximum magnetic induction normal to the surface for a sea-water plate is forty-four times as great as it would be for an iron plate, and more than three thousand times as great as it would be for a copper plate. The paper also shows that, for the purpose of induction telegraphy, to get the best effect the receiving coil should have its plane vertical—not horizontal; firstly, because the distance of the in-

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ducing circuit from the surface of the plate must in practice be small compared with the distance of the point from the axis, so that the maximum normal induction is small compared with the maximum tangential induction; and secondly, because the maximum *normal* induction varies inversely as the *fifth* power of the distance of the point from the axis, whereas the maximum tangential induction varies inversely as the fourth power of that distance. In conclusion, Mr. Whitehead applies his formulæ to the practical case mentioned by Prof. Lodge in the *Journal of the Inst. of Electrical Engineers* (Feb., 1899, p. 805). Prof. Lodge there describes a horizontal receiving circuit, and states that, with no condensers in the circuit, he "was not usually able to hear anything" in the telephone. Mr. Whitehead calculates that under such conditions the theoretical value of the current in Prof. Lodge's horizontal secondary is 0·066 *micro*-ampères, but that with a vertical circuit the received current would have been 33 *milli*-ampères.

Mr. Blakesley observed that, as a rule, experiment preceded theory. He congratulated Mr. Whitehead upon having settled from theoretical considerations that the vertical position of the receiving coil is best.

Prof. Everett said that the very elaborate method of analysis adopted in the paper appeared to be very clearly stated. He would like to know whether the inducing coil ought to be vertical as well as the receiving coil.

Mr. Appleyard thought that experiment had left no doubt as to the best position of both coils. The early investigations of Mr. Willoughby Smith and the later work of Mr. H. R. Kempe and Mr. Preece had proved that for the best effect both coils should be vertical. But large vertical coils were difficult to fix and expensive to maintain. It was this reason probably that led Prof. Lodge to try what could be done with coils placed horizontally.

Mr. Whitehead, in reply, said that his formulæ only applied to a horizontal inducing coil. He had not worked out the case of what would happen if the inducing coil itself was vertical. In the Flat Holm experiments both circuits were straight wires with their ends to earth, so that they really amounted to vertical coils.

Mr. R. A. Lehfeldt then gave a demonstration of a method due to Prof. T. W. Richards for standardising thermometers. This depends upon the ordinary latent-heat principle for maintaining constant temperature, but it includes the consideration of generally more than two states or phases of the melting substance. If there are c components and p phases, then the number of degrees of freedom of the system is $[c+2-p]$. When this is zero, the temperature and the pressure of the system are perfectly definite. Thus the following chemical formula represents the four phases to be equilibrated in the case of Glauber's salt:—

$$\left\{\begin{matrix}Na_2SO_4 10H_2O\\ Na_2SO_4\\ \text{Solution}\\ \text{Vapour.}\end{matrix}\right.$$

Prof. Richards has determined the temperature of equilibrium in several useful cases. The salts are put into a test-tube in an air-bath formed between it and a second test-tube; the whole is then heated in a beaker of water over a small flame. If the salt is pure, and care is taken to avoid the effect of supersaturation, this method is highly satisfactory. It gives an extensive range of fixed-points, and is especially useful in thermometry for fixed-points between 0° and 100°. A few of these temperatures may be noted:—

Sodium chromate	19·71° C.
Sodium carbonate	53·3
Sodium thiosulphate ..	48·0
Sodium bromide	50·8
Manganese chloride ..	57 8
Trisodium phosphate ..	73·4
Barium hydroxide	78·0

Mr. J. A. Harker asked how long the temperature remained constant. The special value of Richards's method for standardising thermometers of short range had been pointed out by Dr. Chree. It obviated the necessity for auxiliary bulbs, and it would be extremely useful in graduating meteorological thermometers.

Mr. Blakesley said that sodium chromate was represented by a very useful temperature. Could this substance be regarded as sufficiently stable to give a satisfactory fixed-point?

Mr. Lehfeldt, in reply, said that the time taken by the transformation was certainly several hours. All the fixed points mentioned were theoretically as definite as that corresponding to sodium sulphate, but they had not been so accurately determined.

NOTICES OF BOOKS.

Precious Stones and Gems: their History, Sources, and Characteristics. By Edwin Streeter, F.R.G.S., M.A.I., Gold Medallist of the Royal Order of Frederic, Holder of a Gold Medal from H.M. the King of the Belgians. Sixth Edition, Revised, and largely Re-written, up to date. London: George Bell and Sons, York Street, Covent Garden. 1898.

This beautifully illustrated volume is probably the most complete treatise that has yet appeared on the subject of precious stones. The present issue has been subject to revision, and contains the latest information on the history and properties of gems. From an author whose enthusiasm is so well known it could not fail to be both interesting and valuable. In his preface the author points out that the science of gems must necessarily include a competent knowledge of crystallography, physics, chemistry, and geology, but there are for the identification of precious stones several simple but valuable means which admit of application without any profound knowledge of mineralogy, and these tests have been included in an Appendix at the end of the book.

The need on the part of the jeweller of a sound knowledge of the properties of gems is amply illustrated by the following incident:—Some family jewels, consisting of a sapphire and diamond suite that had passed the probate several times, and had been valued by one of the first jewellers of the day, were handed to the author to report upon, and after examination he had the unpleasant duty of informing the unfortunate legatee that the *sapphires* were only paste! Had they been genuine they would have been worth from £30,000 to £40,000.

A considerable section of the book is naturally occupied with the history and properties of the diamond, and includes some interesting and little-known facts. In the early days of the present African mines, when much scepticism was abroad as to the genuineness of the mines, Mr. Streeter cleared up the doubts of many by sending out a representative, who not only purchased and reported upon the stones, but also acquired considerable interest in the workings. It is remarkable that public recognition of South African diamonds was so long withheld, although it appears certain that the presence of diamonds was known to European colonists as early as the middle of last century. In a mission map, dated 1750, the words "here be diamonds" are to be seen inscribed across the territory of Gricqualand West. The old Dutch residents of Cape Town were also well acquainted with the fact, but very little was heard about the matter until about thirty years ago, when chance brought to light, at a farm near Cape Town, a very fine crystal, which ultimately found its way to the Paris Exhibition, and so public attention was directed to the matter.

Of all the popular errors that have surrounded the diamond, one of the most astonishing—because it has

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hardly disappeared even at the present day—is that it cannot be broken by a hammer! Through this ignorance many a fine crystal has been lost. Pliny, in an account of the diamond, asserts "that the superiority over fire and steel is subdued by goats' blood, in which it must be soaked while fresh and warm, and then only when the hammer is wielded with such force as to break both it and the anvil will it yield."

Passing on to historical diamonds, drawings are given of the famous Koh-i-nur both before and after re-cutting; it is remarked that the ancients did not appreciate the art of the lapidary so highly as we do, and would have been horrified at sacrificing 80 carats of a stone weighing 186 carats, as in the re-cutting of the Koh-i-nur, and one cannot help thinking that the horror is not exclusively confined to the ancients. In many quarters the wisdom of converting the famous "mountain of light" into a modern brilliant of less than two-thirds its original weight has been questioned.

A remarkable story is told of the Agra or Delhi diamond—a pink stone of very great beauty—and the manner of its transference to England. Certain young officers in the regiment at Delhi having obtained possession of the stone, determined to smuggle it home, and so escape sharing its value as loot. After many suggestions one of them hit on the bright idea of enclosing it in a horse ball, and causing one of the regimental horses to swallow it. Having reached the port of embarkation the innocent smuggler was "taken ill," and had to be shot, and the stone having been removed from its stomach was brought to England. It has since been re-cut, and its weight reduced from 46 carats to 31½.

The beautiful "Eugene" diamond that was sold for a very large sum to the Emperor Napoleon III. is recorded to have been first found by a poor Indian peasant, who offered it to the village blacksmith in return for repairing his plough. The blacksmith valued it so lightly as to fling it away, but afterwards, thinking better of it, picked it out of his rubbish heap, and ultimately succeeded in selling it for 6000 rupees!

Perhaps the most important of all coloured diamonds was the famous blue stone once the property of Louis XIV., which appears originally to have had the form of a large drop or pendant. During the troublous times of the Revolution in 1792 this gem vanished, and has never since been found; but in 1830 a very fine blue brilliant, of some 23 carats weight, came to light without a history. Subsequently a small blue drop-shaped stone, of identically the same colour, was purchased in Geneva, and finally a still smaller blue stone was bought in Paris by the author. These three stones exactly accounted for the lost gem.

Passing from historical diamonds, an account is given of the occurrence of minute diamonds in the meteorites of the Canyon Diablo in Arizona, first recognised by Mr. A. E. Foot, of Philadelphia, and since confirmed by many observers; and the theory that the diamond deposits or pipes of the Kimberley mines are of meteoric origin is discussed. The property of phosphorescence in the diamond is very marked; exposure to bright light for a few minutes causes some stones to shine brilliantly in the dark. The author mentions an instance of an orange-coloured stone which, after exposure to lime-light, became sufficiently luminous to light up a room. Reference is made to the beautiful property of diamonds, first pointed out by Sir William Crookes, of phosphorescing under molecular bombardment *in vacuo*, as well as the more recent observation of its great transparency to Röntgen radiation.

The section closes with a short description of the best-known African mines, and a full-sized drawing of the "Excelsior" diamond, of 970 carats weight, from the Jagersfontein mine, now in process of cutting at Amsterdam. A good description is given of the mines, and methods of working in India, Brazil, Borneo, Australia, and America. This last country is responsible for an attempted gigantic fraud. In the year 1870 large discoveries of diamonds were reported from Arizona; but it was eventually found that the ground had been "salted" with diamonds and other precious stones, purchased in England for that purpose!

In connection with the ruby mines of Burma, the author tells a story that shows in strong relief the energy and perseverance necessary to carry on an enterprise of this kind, and, in spite of the disappointing results that seem to have attended the operations of the present ruby mines, hopes are held out of better things in the future.

There are few gems more associated with romance and superstition than the opal. As described by Nichols, two and a half centuries ago, "The opal is a precious stone which hath in it the bright fiery flame of the carbuncle, the fine refulgent purple of an amethyst, and a whole sea of the emerald's green glory; and every one of them shining with an incredible mixture and very much pleasure." Pliny describes an opal valued at £20,000 of our money, the property of Senator Norius, who was proscribed by Marc Antony for the sake of this gem, but, making his escape, carried it with him as the sole relic of his fortune, preferring exile with his opal to life in Rome without it.

In connection with agates it is mentioned that very fine coloured ones are produced by the method of dyeing, *i. e.*, steeping the stones in various metallic solutions and then heating: one process is to soak the stones in an aqueous solution of honey and afterwards in sulphuric acid, and, finally, strongly heating, whereby the volatile products are removed and carbon deposited in the porous parts of the stone, producing many fine effects.

The illustrations given in the volume are very good, both for mineralogical accuracy and beauty; and at the end of the book there is a classification of precious and semi-precious stones under seven separate heads, according to their chemical composition. This cannot fail to be of value to any one interested in precious stones, whether as amateur or professional.

OBITUARY.

PROFESSOR C. FRIEDEL.

We regret to announce the death of M. Charles Friedel, Dean of the Chemical Section of the French Académie who died at Montauban, after a very short illness, on Wednesday, April 19th, at the age of sixty-seven.

At the meeting of the Académie on April 24th, the President referred to their recent loss in the following terms:—

M. Friedel was a pupil of Würtz, whom he succeeded in the Chair of Organic Chemistry at the University of Paris. All his efforts were devoted to continuing and developing the work of his illustrious master and friend. By his numerous and important researches, which opened the doors of the Académie to him in 1878, and by the distinguished pupils which were trained in his laboratory, he exercised a great influence on the progress of organic chemistry in France throughout the last quarter of a century. It would be well for others to follow, one by one, all the stages of this active scientific life.

This sudden and unexpected departure of our colleague will be nowhere felt more than in our Académie, where we have appreciated—above all, in that it extended scientific research—the amiability of his person and the uprightness of his character, indefatigably upholding justice and truth.

In the assurance that I am interpreting the sentiments of all, in rendering to him this last homage, I close this meeting as a sign of mourning.

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CORRESPONDENCE.

LABORATORY GAS FURNACE.

To the Editor of the Chemical News.

SIR,—Our attention has been drawn to a note in the CHEMICAL NEWS of March 17th (vol. lxxix., p. 131) stating that the Holloway Patent Furnace—of which we are makers, and of which you gave a notice on September 23rd, 1898, p. 157—is "almost identical with one that Messrs. Fletcher, Russell, and Co. inform us has been made by them for the last fifteen or twenty years." With this we cannot agree. The shape and size are practically identical—because they are the most convenient, and could not well be different—but the construction is entirely new.

The Holloway furnace body is made in two parts, which increases its portability and renders it cheaper and less liable to crack. The base extends forward and forms a table in front of the furnace; the body has no side flanges extending beyond the base or top, so that the doors cannot get jammed. The deep flanges on the doors prevent them from falling down; and the burner is of a new construction. All these features add to the value and convenience of the furnace very considerably, and render it entirely different to previous forms.—We are, &c.,

JOHN J. GRIFFIN & SONS, Lim.

20—26, Sardinia Street, Lincoln's Inn Fields,
London, April 26, 1899.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

NOTE.—All degrees of temperature are Centigrade unless otherwise expressed.

Comptes Rendus Hebdomadaires des Séances, de l'Académie des Sciences. Vol. cxxviii., No. 15, April 10, 1899.

New Method of Preparation of Iron Silicide, SiFe.—P. Lebeau.—The author employs silicide of copper as a solvent for silicide of iron, which allows of the preparation of the compound SiFe in a well crystalline form. He also proves that at a high temperature copper silicide dissociates, and is capable of yielding its silicon to another metal, such as iron, which has a greater affinity for silicon than the original copper. This reaction can be applied to the preparation of other metallic silicides; the author having verified the reaction in the case of the silicides of cobalt, nickel, and chromium. The employment of the arsenides and stibnides of copper has led to comparable results. The author proposes to continue the investigation of these binary compounds by this new method.

Preparation and Properties of a Crystalline Subphosphide of Copper.—Georges Maronneau.—M. Moissan showed that, by the reduction of calcium phosphate by carbon in the electric furnace, crystalline phosphide was obtained. The author extends this method to the preparation of other phosphides. By the reduction of copper phosphate by carbon in the electric furnace, he obtains a phosphide of copper in a crystalline form, having the formula Cu_2P. This compound has density 6·4. When heated in a current of hydrogen to a temperature of 1000°, the phosphide loses a small quantity of phosphorus, and becomes a grey powder; it is attacked slowly by acids in the cold, except nitric acid; it is completely soluble in hot nitric acid. Heated slightly in oxygen, it oxidises. In the presence of fusing sulphur, formation of copper sulphide takes place with incandescence.

Thermic Properties of Lime Prepared at Different Temperatures.—Henri Gautier.—The rapidity of hydration of lime varies considerably with the conditions of temperature at which it is obtained. Lime prepared at 1000°, thrown into a large quantity of water, unites so rapidly as to vaporise some of the water; when prepared at 1300°, it is attacked quietly; and extremely slowly if prepared at a much higher temperature in the electric furnace. The author has investigated these reactions, to find whether these differences in the rapidity of hydration are due to a difference in the molecular state of the chalk when prepared at different temperatures. He used pure lime prepared by the calcination of Iceland spar. His results show that the amount of heat developed is the same in all cases.

Berichte der Deutschen Chemischen Gesellschaft. Vol. xxxi., June 27, 1898.

On the Heat of Volatilisation of some Elements, and on their Molecular Weight in the Liquid State.—J. Traube.—The formula given by Clausius,—

$$\rho = T\frac{dp}{dT}(v_1 - v_2),$$

in which ρ is the latent heat of volatilisation, T the boiling-point in absolute degrees, v_1 and v_2 the specific volumes of the vapour and of the liquid at the temperature T, enables us to calculate, after integration, the molecular weight in the liquid state. By applying this equation we find that the elements Br, I, Zn, Cd, Hg, and Bi have the same molecular weights in the liquid and gaseous states (Zn, Cd, Hg, and Bi are monatomic, Br and I are diatomic). Sulphur is an exception. The above formula can be replaced by that of Trouton, of which it is the definite integral at the normal pressure, $\frac{m\rho}{T} = 20{\cdot}63$. The values of ρ given by this last equation do not coincide with those furnished by the first formula except when the elements have the same molecular complexity in the liquid and gaseous states.

Spectro-chemistry of Nitrogen (continued).—J. W. Brühl.—Nitrosobenzene gives optical constants leading to the double formula $C_6H_5{-}N{-}O$ / $O{-}N{-}C_6H_5$. Nitrosochloride of tetramethylethylene has similar anomalies, and should have one of the following constitutions:—$(CH_3)_2.C{-}C(CH_3)_2$ / $N.OCl$ or $(CH_3)_2.C{-}C.(CH_3)_2$ / $ClN{-}O$. Phenylhydroxylamine has the generally accepted formula C_6H_5NHOH. The oxygenated ethers of dinitrobenzene have an abnormal refraction. Nitrourethane should be classed among the nitramides, and have the constitution

$$C_2H_5OCO.NH{-}N\begin{matrix}O\\ \diagup\\ \diagdown\\ O\end{matrix}$$

Some Double Glycerolates of Copper and the Alkaline Metals.—F. Bullheimer.—Glycerolate of copper and sodium, $(C_3H_5O_3CuNa)_2 + C_2H_5OH + 9H_2O$, is obtained by two methods:—By the first way, we dissolve 5 grms. of cupric hydrate in 3 grms. of glycerin containing 3 grms. of NaOH and 15 c.c. of water; we then add 50 c.c. of alcohol, filter, and add more alcohol until the cloudiness is persistent. By the second method, 150 c.c. of an alcoholic solution of acetate of copper saturated at 60°, are added to 50 c.c. of water, 6 grms. of glycerin, and 100 c.c. of ethylate of soda (containing 5 grms. of Na); add 100 c.c. of alcohol, and allow to cool. We thus obtain blue prismatic needles, which lose their alcohol and part of their water (6 mols.) *in vacuo*. The methods of preparing the glycerolates $C_3H_5O_3CuNa.3H_2O$ and $C_3H_5O_3CuLi.6H_2O$ are also described. These two products crystallise in hexagonal blue tables.

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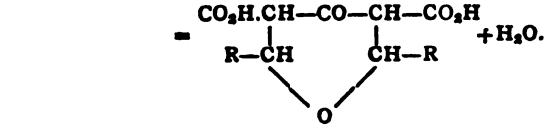
New Oxidation Product of Theobromine.—H. Clemm.—The oxidation of theobromine by means of HCl and $KClO_3$ gives an oxydimethyluric-3.7 acid, analogous to the oxy-β-dimethyluric acid obtained by Fischer by oxidising β-dimethyluric acid by the same process. Oxydimethyluric acid crystallises in the form of thin plates, fusible with decomposition at about 201—203°, slightly soluble in water and the cold organic solvents, also in the alkalis. Boiling baryta-water splits this acid up into mesoxalic acid and methylurea.

Action of Nitroso-carbides on Concentrated Sulphuric Acid.—E. Bamberger, H. Busdorf, and H. Sand.—Concentrated sulphuric acid reacts instantaneously on nitrosobenzene at 0°. If the raw product is diluted with water, we obtain a yellowish precipitate which crystallises in boiling alcohol in thin bronze plates. This body corresponds to the formula $C_{12}H_{10}N_2O_2$; it melts at about 152°, decomposing brusquely, and dissolves easily in chloroform and warm acetone; it is slightly soluble in benzene, ether, and ligroin, and insoluble in water. Reducing agents transform it into *p*-aminodiphenylamine. The authors have also given it the formula of a *p*-nitroso-diphenylhydroxylamine, $C_6H_5.N(OH).C_6H_5.NO$. Several derivatives are described, such as the monacetyl, the *p*-nitroso-di-*o*-tolylhydroxylamine, &c.

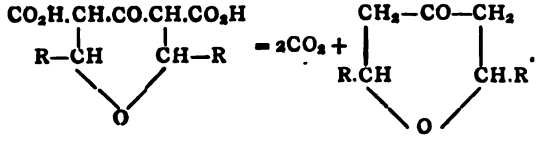
Action of Phenylhydroxylamine on Aniline and on Sulphuric Acid in the presence of Alcohol.—E. Bamberger and Jan. Lagutt.—When we heat a mixture of phenylhydroxylamine (100 grms.), absolute alcohol (2400), and sulphuric acid (50 c.c.) for twenty-four hours on a water-bath, we obtain the following products:—Nitroxybenzene (14 grms.), *p*-phenetidine (45·8 grms.), *o*-phenetidine (8 grms.), *p*-aminophenol (3·5 grms.), *o*-aminophenol (3·5 grms.), aniline (4 grms.), nitrophenol, phenol, &c. (traces). In the cold we only obtain nitroxybenzene, aniline, and *p*-amino-phenol. In no case were the authors able to isolate the compound $C_6H_5.NH.OC_2H_5$. The authors have also studied the action of aniline on phenylhydroxylamine. A solution of 75 grms. of phenylhydroxylamine in 100 grms. of aniline, was gradually added to a solution of hydrochlorate of aniline (105 grms.) in 130 grms. of aniline heated to 130°. At the end of one hour the phenylhydroxylamine had disappeared and the mass contained the following products:—Nitroxybenzene (17 grms.), various colouring-matters (19 grms.), sulphate of benzinidine (10 grms.), sulphate of *p*-aminodiphenylamine (8·6 grms.), *o*-aminodiphenylamine (6·4 grms.), chloraniline (traces). In another experiment, *p*-aminophenol was also obtained.

Derivatives of Tetrahydropyrone.—P. Petrenko-Kritschenko.—The aromatic aldehydes react easily on ether or acetone dicarbonic acid, giving rise to very slightly stable intermediate products, which themselves lose carbonic acid while being transformed into tetrahydropyrone derivatives:—

$$CO_2H.CH_2.CO.CH_2.CO_2H + 2R.CHO =$$

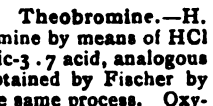


$$= \text{(above)} + H_2O.$$



$$= 2CO_2 +$$

The stability of these pyronic derivatives is very variable. Dimethoxydiphenyltetrahydropyrone,—



is obtained by saturating a mixture of acetone dicarbonic acid (1 mol.), methylsalicylic aldehyde, and acetic acid with hydrochloric acid gas. The product is dissolved in Na_2CO_3 and precipitated with HCl. We thus obtain the corresponding dicarbonic acid which loses CO_2 at the temperature of the water-bath.

MISCELLANEOUS.

Drown's Method of Determining Silicon.—A. C. Langmuir.—In the July number of the *Journal of the American Chemical Society*, George Auchy has described a method devised by him, which will effect a more thorough dehydration of the silica than is obtained by the method usually followed. Dr. Dudley (*Journ. Amer. Chem. Soc.*, xix., 106) called attention to the difficulty of dehydrating in this case at the Troy meeting of this Society in 1896. Without claiming any superiority over Mr. Auchy's method, it may be of interest to describe a modification which has been in use in this laboratory for a number of years. It is not original with the author. The pig iron or steel is weighed into a No. 4 beaker, and brought into solution by the usual method as described by Blair. We then add 40 c.c. of concentrated sulphuric acid, and evaporate to fumes on the hot plate. A leather strap, about 1 inch broad and 20 inches long, is passed under the lip of the beaker, and the ends clasped between the thumb and forefinger. By a slight wrist movement the contents of the beaker are given a rapid rotary movement. The beaker can, in this way, be heated directly in the full flame of the Bunsen burner with perfect safety. Care only must be taken that the contents are kept in continual motion, and that sufficient acid is present to cover the glass exposed to the flame. Under these circumstances any lumps are broken up, and a thorough contact between the silica and the very hot acid is insured. In many other cases where evaporation to fumes is necessary, and the tendency to bump prevents the simple boiling down of the solution, the use of a strap in this way is invaluable. As a rule it will be found more convenient than the use of the casserole. It is also very convenient in handling hot beakers, as it is adaptable to one of any size. We perhaps run the risk of recounting what may be to some chemists an old story, but, as in our experience we have yet to visit a laboratory in which the strap was used in this way, it is but reasonable to conclude that it has not met with the attention it deserves.—*Journ. Amer. Chem. Soc.*, xxi., No. 2.

MEETINGS FOR THE WEEK.

MONDAY, 8th.—Society of Arts, 8 (Cantor Lectures). "Leather Manufacture," Prof H. R. Procter, F.I.C.
—— Royal Institution, 5. General Monthly Meeting.

TUESDAY, 9th.—Royal Institution, 3. (The Tyndall Lectures). "Electric Eddy-currents," by Prof. Silvanus P. Thompson, D.Sc., F.R.S.

WEDNESDAY, 10th.—Society of Arts, 8. "Fruit Growing in Kent," by George Bunyard.

THURSDAY, 11th.—Royal Institution, 3. "Embroidery," by Lewis F. Day.
—— Society of Arts, 4.30. (Indian Section). "Agrarian Conditions under British and Native Rule," by Michael Francis O'Dwyer, I.C.S.

FRIDAY, 12th.—Royal Institution, 9. "Magnetic Perturbations of the Spectral Lines," by Prof. Thomas Preston, M.A., D.Sc., F.R.S.

SATURDAY, 13th.—Royal Institution, 3. "To Iceland in Search of Health" (with Lantern Illustrations), by W. L. Brown, L.R.C.P., L.R.C.S.

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THE CHEMICAL NEWS.

Vol. LXXIX., No. 2059.

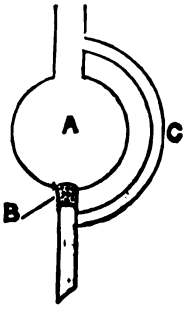
ON SOME NEW APPARATUS.

By F. W. ASTON.

Having occasion to prepare large quantities of pyromucic chloride for some research in which I am at present engaged in conjunction with Prof. P. F. Frankland, new forms of apparatus were devised, and, as they may be of some service to other experimenters, they are here described.

I. *A Chlorinating Apparatus.*

Owing to the comparative insolubility of pyromucic acid in chloroform, its reaction with PCl_5 in this solution, using the ordinary apparatus, is very inconvenient. The following apparatus, however, avoids all choking of the condenser, works automatically, and at the same time allows of the use of crude acid.



The apparatus is made of glass, and is of the simple form shown in the accompanying sketch. The crude acid is placed in the bulb A, being prevented from falling out by a plug of glass-wool, B. A flask, containing the PCl_5 and chloroform, is attached to the lower extremity, and a reflux condenser is fitted to the upper. On boiling the contents of the flask on a water-bath, the chloroform distils up the side tube C, and, being condensed, flows back through the bulb into the flask, drop by drop, saturated with acid, being freed from all tarry and other insoluble matter by the glass-wool; here it reacts with the PCl_5 in the usual manner.

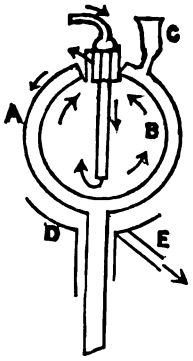
By means of this arrangement the reaction is rendered perfectly smooth, and needs practically no attention when once set at work.

II. *New Form of Condenser.*

With the above apparatus I have used a new form of double surface condenser, very suitable on occasions where a reflux condenser is required, and possessing advantages over condensers previously described by reason of its great efficiency. It is made of glass, in the form shown in the accompanying sectional sketch.

It consists of an outer bulb, A, from a thickened part of which is formed by suction a very thin concentric inner bulb, B, through which the cooling water circulates as indicated by the arrows, subsequently flowing in a thin stream over the outer surface of the bulb A into the cup D, and running to waste through the escape tube E.

The spherical shape of the condenser and its peculiar method of construction enable the inner bulb to be made of exceedingly thin glass, without fear of breakage and render the effective cooling surface enormously great compared with the space occupied. As the side tube C is joined on at the thickest part of the bulb, the structure is rendered very strong and rigid.



For reflux work it is most convenient to have the side tube pointing upwards, as in the figure, but if it is fused on at an angle the condenser can be used for ordinary distillations, and has the advantage of taking up very little bench space.

Mason University College, Birmingham,
April 28, 1899.

ON THE PRODUCTION OF CRYSTALLISED TUNGSTEN BY ELECTROLYSIS.

By L. A. HALLOPEAU.

I have already shown, in previous papers, the reducing action of hydrogen and tin on melted paratungstate of lithium.

Tin reacts on this salt, giving a tungstolithic tungstate. With hydrogen the reduction is more complete; we obtain at a red heat crystallised binoxide of tungsten, which at a higher temperature would be itself reduced to the metallic state.

Following up these experiments, there remained to study the action of electrolysis on melted tungstate of lithium. The electrolysis of the paratungstates of sodium and potassium gives rise to alkaline tungsto-tungstates; with the lithium salt the result is different.

Paratungstate of lithium, melted in a porcelain crucible and carried to a temperature of about 1000°, was submitted for three hours to the action of an electric current of 3 ampères and 15 volts; the electrodes were of platinum. The melted mass was treated successively with boiling water, concentrated hydrochloric acid, and a boiling solution of lithia at about 20 per cent; after a final washing with warm water there remains a distinctly crystalline substance. This is tungsten mixed with a certain amount (up to 6 per cent) of platinum; the platinum comes from the electrodes which are attacked by the melted lithia.

Tungsten thus obtained is in the form of opaque crystals, having a beautiful metallic lustre and a prismatic appearance. As a rule these crystals take the form of needles, which have some resemblance to the needles of silicon; they might very well be piled up octahedra, as is the case with silicon.

To analyse this substance it suffices to submit it to the action of a current of oxygen at a red heat, so as to burn all the tungsten, which is transformed into tungstic acid. The product of the oxidation is then melted with carbonate of soda. The melted mass is re-dissolved in water, and filtered to separate the platinum; in the filtrate the tungstate acid is precipitated in the form of

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mercurous tungstate. As a check, the increase in weight resulting from the oxidation of the material in the current of oxygen should be equal to the theoretical weight of the oxygen necessary to transform the tungsten present into tungstic acid. This method allows of the rapid analysis of all the products of reduction of the acid tungstates, oxides of tungsten, and alkaline tungsto-tungstates.

Zettnow has already obtained metallic tungsten by passing an electric current through melted tungstate of sodium, but the tungsten prepared by this method was black and powdery. Most of the methods tried for the preparation of tungsten also give amorphous products. Wöhler's method, which consists of reducing the acid tungstate of potassium by a current of hydrogen, alone furnishes crystalline tungsten: by the aid of a very powerful glass I was able to distinguish, in the midst of these crystalline grains, a few crystals in the form of needles, which very closely resembled those of the tungsten obtained by the electrolysis of the paratungstate of lithium.

I have not succeeded in electrolysing the paratungstate of lithium with iron electrodes, this metal being attacked very readily by the melted salt. I propose repeating the experiment, using iridio-platinum electrodes. In any case the electrolysis of the paratungstate of lithium only enables us to obtain very small proportions of the metal; the only method by which large quantities can be obtained is that of M. Moissan, who has shown that, with the help of the electric furnace, we can prepare melted tungsten in a state of absolute purity.—*Bull. Soc. Chim.*, Series 3, vol. xix.-xx., No. 24.

HYPERBORATES AND HYPERTITANATES.

By P. MELIKOFF and L. PISSARJEWSKI.

Hyperborate of ammonium, $NH_4BoO_3+\frac{1}{2}H_2O$, is prepared by dissolving boric acid in an aqueous solution of peroxide of hydrogen at 2·5 per cent, adding ammonia, and precipitating the salt with alcohol. This salt occurs in white crystals, very stable when dry. In the same manner as hyperborate of soda, already described (*Berichte*, xxxi. [4], 678), it gives off peroxide of hydrogen when treated with dilute sulphuric acid, ozone when treated with concentrated sulphuric acid, and chlorine when treated with hydrochloric acid. It dissociates in aqueous solution at the ordinary temperature, but more rapidly at 45° C., giving off oxygen and forming nitrate of ammonia. The freshly precipitated salt contains 3 molecules of water of crystallisation, but after having been kept over sulphuric acid for twenty-four hours it only retains half a molecule.

The barium salt, $Ba(BoO_3)_2+7H_2O$, is prepared by the double decomposition between a saturated solution of the soda salt at 0° C. and a solution of chloride of barium. It is difficultly soluble in water, and behaves like the ammonium salt when treated with acids. It decomposes slowly at the ordinary temperature.

The calcium salt, obtained in an analogous manner, is much less stable in water than the barium salt, and it is equally insoluble.

The insoluble hyperborates of nickel and of copper, obtained by the action of the sulphates of these metals on the soda salt, decompose rapidly with the evolution of oxygen. It is due to this circumstance that their analysis has not been effected.

By the action of chloride of cobalt on hyperborate of soda, we obtain the peroxide CoO_2,CoO, with evolution of oxygen. The salts of manganese give an analogous reaction.

Every attempt to obtain compounds of hyperboric acid with the metallic peroxides has been unsuccessful.

Hypertitanic acid forms, with the metallic peroxides, not only basic salts of the type $(R_2O_2)_2TiO_3$, but also neutral salts of the type $R_2O_2.TiO_3$.

Hypertitanate of normal peroxide of sodium, $(Na_2O_2.TiO_3+3H_2O)$, is obtained either by the action of peroxide of hydrogen and caustic soda on titanic acid, and the decomposition of the solution by alcohol, or else by the decomposition of the basic salt by means of water. In one and the other case a thick oily liquid separates, which changes into a yellow powder by desiccation over sulphuric acid. Treated with dilute sulphuric acid, this salt gives off peroxide of hydrogen; it also decomposes hydrochloric acid with the liberation of chlorine.

The hypertitanate of peroxide of ammonium, $(NH_4)_2TiO_3.H_2O_2$, is prepared by pouring a solution of peroxide of hydrogen over hypertitanic acid, adding ammonia and precipitating the salt by alcohol. This salt crystallises in small yellow prisms. It is fairly stable in the dry state, but dissociates in aqueous solution with the evolution of oxygen. It detonates slightly when heated over a flame. Dilute sulphuric acid and hydrochloric acid act on it as on the soda salt.

The hypertitanate of the normal peroxide of barium, $BaO_2.TiO_3+5H_2O$, is prepared by double decomposition between the soda salt and chloride of barium. Dried over sulphuric acid it appears as a yellow powder.—*Berichte*, xxxi. [7], p. 953.

A NEW HYDRATE OF THE SALINE OXIDE OF CHROMIUM.

By G. BAUGÉ.

The various double carbonates of protoxide of chromium, of which we have already described the preparation and properties, all gave the same reaction with boiling water. All the carbonates, in fact, when treated with boiling water and protected from contact with the air, gave a hydrated oxide of chromium which was shown by analysis to be a saline oxide containing 3 molecules of water.

Peligot (*Ann. Chim. Phys.*, Series 3, vol. xii., p. 539) has already shown the existence of a hydrate of the saline oxide containing 1 molecule of water. The hydrate I have obtained is thus different to that which has been described by Peligot. I therefore propose to describe its preparation and properties.

Preparation.—We used the same apparatus that served for the preparation of the double salt of sodium, but replacing the tubulated flask with a flask closed with a cork giving passage to two easily fitting tubes bent at right angles. This apparatus was traversed by a current of carbonic acid free from oxygen, a certain quantity of one of the double salts of protoxide of chromium* was placed in the flask; then, by means of the tubes, boiling water was poured on to the product, and the boiling kept up for about half an hour. Directly the water is added the salt decomposes, losing carbonic acid and hydrogen; but it is important, for the rapid termination of the reaction, to boil for some time, as mentioned above. The mixture is then passed, while still agitating, to the filtering-tube which terminates the apparatus; then, with the aid of a filter-pump, we wash the product with boiling water until the washings are no longer precipitated by chloride of barium.

In this manner we obtain a brick-red body, which is dried at 100° in the tube itself. During this desiccation we notice that this body changes colour, and becomes yellowish brown while losing water. This transforma-

* The best results were obtained with the double salt of potassium. We can even proceed without first preparing the double salt; it suffices to have in the flask the necessary ingredients for making this salt.

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tion occurs gradually in the direction of the entrance of the current of gas, and the surface of the separation of the two layers is quite distinct.

If the separation is stopped before the completion of this change, we can, after cooling, remove from the immediate neighbourhood of the surface of separation portions of the brick-red body.*

Analyses made on samples from several experiments cause us to believe that this unstable brick-red body is a hydrate of the saline oxide, containing 4 molecules of water.

The Yellow-brown Hydrate. — This substance can be most rapidly obtained by closing one end of the tube containing the brick-red body, placing it in boiling water, and making a vacuum by the other end, until it no longer loses water.

Properties.—This hydrate cannot be confounded with the former one. In fact, if it is placed in the presence of boiled water, in an inert atmosphere, it remains a yellow-brown. Further, even after a month, it does not regain the water of hydration which it lost. It occurs in the form of a yellow-brown powder, with a density of 3·49. Heated *in vacuo*, in a current of steam, hydrochloric acid gas, or an inert gas, it gives, at about 250°, sesquioxide of chromium with a loss of hydrogen, but without incandescence.

It is attacked by chlorine at a dull red heat with the evolution of steam, subchloride of chromium, and hydrochloric acid gas: this class of reaction has already been noted by M. Moissan. Though fairly stable in dry air, it oxidises rapidly in the presence of water. This oxidation is the more lively as the compound has been the more recently prepared. Heated in air, it then gives sesquioxide of chromium without incandescence. Sulphuretted hydrogen below a red heat transforms it into a crystallised sulphide. It is an energetic reducing agent. When placed in contact with dilute sulphuric acid it reduces it at about +40°. This reduction may go on to the formation of sulphuretted hydrogen if the oxide is added in sufficient quantity..

Treated warm with concentrated hydrochloric acid it gives a mixture of chromous and chromic chlorides. The formation of the chromous salt may be shown in the following manner:—We place anhydrous sesquichloride of chromium and concentrated hydrochloric acid in a tube traversed by a current of carbonic acid, and boil; no solution takes place. If we now add a small quantity of the saline oxide, the sesquichloride goes rapidly into solution. We know that this solution is characteristic of the salt of protoxide of chromium. All efforts to effect complete dehydration without decomposition, or to obtain Peligot's hydrate, have given no results.

Analysis.—We used the method described by Peligot (*loc. cit.*).

The water given off by a known weight of oxide when heated in a current of dry carbonic acid is weighed; we also weigh the residue, and measure the volume of hydrogen arising from the water decomposed by the oxidation of the protoxide. This method of analysis gives, in a single operation, all the elements required for the calculation. The hydrogen shows, on the one hand, the weight of oxygen necessary to cause the oxide under examination to pass to the state of sesquioxide; on the other hand, the quantity of water which corresponds to it, and which, added to that collected in the tube, gives everything constituting the hydrate, and, subtracted from the weight of the material used, gives the weight of the anhydrous oxide. The weight of the sesquioxide formed controls the preceding results.

This method has given us the following results, expressed in parts per cent:—

	H_2O collected and weighed.	H collected at 0° and 760 m.m.	Residue, calculated as chromium.
I.	16·55	4075·7 c.c	56·65
II.	16·08	4063·4 ,,	57·19
III.	16·32	4057·7 ,,	56·42
Theory	16·42	4064·5 ,,	56·93

The brick-red compound gave us the following quantities of water:—

I.	II.	III.	Theory.
21·96	22·07	21·12	21·57

To sum up, the saline oxide of chromium is susceptible of several states of hydration:—

1. $CrCr_3O_4.H_2O$, obtained by Peligot.
2. $CrCr_3O_4.3H_2O$, determined by us.
3. A brick-red unstable hydrate, which analysis enables us to consider as containing 4 molecules of water.—*Bull. Soc. Chim.*, Series 3, vol. xxi.-xxii., No. 2.

* We have tried to effect this desiccation at a low temperature, and we thus obtained the yellow-brown body.

A REVISION OF THE ATOMIC WEIGHT OF COBALT.*

Second Paper.—The Determination of the Cobalt in Cobaltous Bromide.

By THEODORE WILLIAM RICHARDS and GREGORY PAUL BAXTER.

(Concluded from p. 209).

Since it would be impossible to calculate the weight of the soluble bromides from the weight of the silver bromide without a quantitative analysis of the two bases present, the effort was made to evaporate the aqueous extract from the reduced cobalt, and to weigh the dried residue directly. In the work upon nickel, this method was necessarily rejected because the spongy nickel was oxidised and went into solution as nickelous hydrate, which could not be removed by filtration. Our spongy cobalt oxidised much more rapidly than the nickel upon treatment with water; but the decantate, upon filtration and evaporation in the air, deposited most of its cobalt as cobaltic hydroxide. The presence of salts of the alkalis greatly increases this oxidation, cobalt which has once been leached being oxidised but little. Heat also increases the oxidation, and so probably does the galvanic action with the platinum dishes which were used wherever possible through the whole course of this investigation.

In view of the colloidal solubility of nickelous hydrate in water, it is probable that cobaltous hydrate possesses the same property. When cobalt is treated with water in the presence of air, the metal oxidises and goes into solution as *cobaltous* hydrate; this is then further oxidised by exposure of the solution to the air and thrown out of solution as *cobaltic* hydrate, which can be filtered off. Since the dissolved cobalt is almost completely removed by this process, it is obviously legitimate to weigh the residue obtained by evaporating the aqueous extract of the reduced cobalt, and thus to obtain directly the amount of impurity present in the metal. This difference of procedure in the two cases is an interesting example of the way in which subordinate side reactions may influence two researches otherwise unusually analogous.

In the next four analyses (5 to 8) the cobalt was leached with the purest hot water in a platinum dish, and the solution, after filtration, was evaporated to dryness. The residue was taken up with water, filtered from the deposited cobaltic hydroxide into a weighed platinum crucible, again evaporated, heated to 130°, and weighed.

* Contributions from the Chemical Laboratory of Harvard College. From the *Proceedings of the American Academy of Arts and Sciences*, vol. xxxiv., No 14, February, 1899.

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That these residues contained cobalt was undoubtedly true, from the fact that they were coloured a pale blue both after evaporation and after heating. During the heating, however, a slight blackening took place, which was due to the oxidation of traces of unoxidised cobaltous hydrate. In order to make sure that all unreduced bromides had been removed from the cobalt by the process of leaching, in each analysis the metal was dissolved by cold very weak nitric acid* and treated with silver nitrate. As not even the faintest cloudiness was ever again visible in these solutions, it was assumed that the soluble matter had been completely removed.

In Analysis 5 the bromine in the residue was determined and the result found to be considerably too low to correspond with the weight of the residue, if calculated as sodium bromide. In order to discover the cause of this discrepancy, an elaborate series of experiments was carried out at the expense of much time and labour. To describe these experiments in full would result only in confusing the mind of the reader. It is sufficient to say that pure spongy cobalt was treated with varying amounts of pure sodium bromide in solution, the conditions being regulated so as to be as nearly as possible like those in the analyses. The following conclusions drawn from these experiments are of great importance.

In the first place, no bromine is lost by the residues either during evaporation or in heating to 130°. The cobalt in the residues may be present in three forms: as cobaltous hydrate which has escaped oxidation, as cobaltic hydrate, and as unreduced cobaltous bromide,† each in exceedingly small amounts. The doubt as to the quantity of each present makes it impossible to apply the correction for dissolved cobalt with any degree of accuracy, and in the table of results no attempt has been made to do so. In the later analyses this cause of uncertainty was removed. This correction within a correction is, however, an infinitesimal of the second order; neglecting it can produce no serious effect upon the accuracy of the final result.‡ In this respect the research upon cobalt differs from that upon nickel, where the amount of hydroxide in the residue was relatively great, owing to the fact that it had not been chiefly eliminated by oxidation during the evaporation.

The possibility of the presence of some other acid than hydrobromic acid in the residues led us to make tests in this direction. Silicic acid was of course the first one to suggest itself. Early in the work one test had been made by subliming about 2 grms. of pure cobaltous bromide from a platinum boat in a current of hydrobromic acid gas. After the sublimation of the bromide the boat was perfectly bright, and gave not the slightest evidence of the presence of any silica. One of the residues was now treated with pure strong hydrochloric acid, heated to 130°, again treated with hydrochloric acid, and filtered. The amount of silica found, 3 one-hundredths of a m.grm., is a negligible quantity. Although the purity of the phosphoric anhydride used for drying our gases had been proven by passing air through a tube filled with the pentoxide into aqua regia, which upon evaporation gave no precipitate with ammonic molybdate, nevertheless one of the soluble residues from the reduced cobalt was tested with the same reagent with a negative result.

Upon examining one of the earlier residues for sulphuric acid, however, a slight precipitate of baric sulphate was formed. The source of this sulphuric acid was hard to discover, but finally it was found that the strong sulphuric acid in some of the drying columns had become discoloured in places by organic matter. This must have led to a slight decomposition of the acid and formation of sulphur dioxide, which was subsequently oxidised to sulphuric acid by the bromine. The amount of sulphuric acid present in the bromide was very small, 3·88 grms. of cobaltous bromide giving only 0·00036 grm. of baric sulphate in one case. As in the instance of nickel, however, this cause of error was wholly eliminated in the later experiments, and no trace of sulphuric acid could be detected in the material used in the last series.

The conclusions to be drawn from these experiments seem to be:—

First.—That our cobaltous bromide was almost if not completely reduced.

Secondly.—That the impurities, which consist of alkaline bromides (with, in some cases, a minute trace of sulphates), can be completely removed by leaching the cobalt.

Thirdly.—That the residue obtained by evaporating the water extract of the cobalt after reduction represents, within an exceedingly small amount, the weight of the impurities.

In the fourth series, during which the truth of this third conclusion was not realised, and a method similar to that used in the nickel research was adopted, the weight of the residue had to be calculated. The basis of calculation was the knowledge obtained from Analysis 5, Series V. Unfortunately this is the only analysis of material similar to that used in Series IV., where both the weight of the residue and the silver bromide obtained from it were determined. Since, however, the use of this analysis causes the average of Series IV. to approach within one part in thirty thousand of the average of Series V. and VI., we may safely assume that the rather meagre data represent with great exactness the real weight of the impurity contained in this Sample I. of cobaltous bromide. In Series V. and VI. the residues were weighed directly, so that this factor was not needed. Below are given the results of the first two series of analyses.

The Atomic Weight of Cobalt.

O = 16. Br = 79·955.

FOURTH SERIES (PRELIMINARY).—$CoBr_2$: Co.

No. of analysis.	Sample of $CoBr_2$.	Observed weight of cobaltous bromide in vacuum.	Observed weight of cobalt in vacuum.	Weight of AgBr found from residue.	Weight of residue calculated from AgBr.	Atomic weight of cobalt.
		Grms.	Grms.	Grm.	Grm.	
1.	I.	5·59216	1·50873	0·00309	0·00193	59 007
2.	I.	4 61944	1·24807	0·00681	0·00426	58·996
3.	I.	3·75291	1·01713	0·01267	0·00793	58·989
4.	I.	3·00645	0·81409	0·00815	0·00510	59·007
					Average	59·000

FIFTH SERIES.—$CoBr_2$: Co.

No. of analysis.	Sample of $CoBr_2$.	Observed weight of cobaltous bromide in vacuum.	Observed weight of cobalt in vacuum.	Weight of residue.	Corrected weight of cobaltous bromide.	Corrected weight of cobalt.	Atomic weight of cobalt.
		Grms.	Grms.	Grm.	Grms.	Grms.	
5.	I.	5·32955	1·44189	0·00761*	5 32194	1·43428	58 996
6.	I.	7·51430	2·02965	0·00644	7·50786	2·02321	58·989
7.	II	2·32910	0·62957	0·00280	2·32630	0 62677	58·973
8.	II.	7·45336	2·01378	0·00642	7 44694	2·00736	59·011
					Average		58·992

* From the residue in Series V., Analysis 5, was obtained 0·01216 grm. of argentic bromide. Hence 0·0010 grm. of argentic bromide corresponds to e 000626 grm. of residue. This factor is used in calculating the results in Series I.

* In a platinum dish this solution takes place with great ease, and with no danger of a loss of bromine. The galvanic action is a great assistance.

† Cobaltous bromide could only have found its way into this residue by having been protected from reduction by enclosure in crystals of sodic bromide. It must have been exceedingly small in amount, if present at all.

‡ This extra cobalt may partly explain why the sum of the total analysis slightly exceeds 100·000 per cent.

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It seemed highly important to us at this point to prepare cobaltous bromide which should be free from every impurity. In the first place the drying apparatus was slightly modified, no strong sulphuric acid being used except in drying the air necessary for sweeping the nitrogen out of the weighing bottle. Dilute sulphuric acid was substituted in every case, and two columns of stick potash followed by one of phosphoric anhydride were inserted beyond this dilute acid. As the porcelain tubes had evidently been the source of the alkaline impurities found, a platinum lining, made by bending a large piece of platinum foil into the form of a cylinder, was provided for the outside porcelain tube (compare with the paper on Nickel, *Proc. Amer. Acad.*, xxxiv., p. 331). The smaller porcelain tube was not used at all, the sublimed material being removed by taking out the foil and unfolding it. Cobalt from Sample III. was then sublimed in the remodelled apparatus from a platinum boat. The material obtained in this way gave results for the atomic weight altogether too high—a circumstance due to large quantities of platinum actually found in the sublimed bromide. Even here a small amount of alkaline impurity existed, having crept in through the crack in the platinum foil. Hence, no more work was done with this material; but renewed precautions were taken to prepare by the older method cobaltous bromide which should contain the smallest possible number and quantity of impurities.

Four analyses were made with this new material, which proved in spite of all our care to contain as much soluble matter as before. The water extracts from these analyses were evaporated in a flat platinum dish, which exposed a large surface of the solution to the air. This served to oxidise completely the dissolved cobaltous hydrate, for the residues did not become grey when heated, and upon the addition of water gave perfectly clear solutions. These residues were faintly blue, the colour being due doubtless to a trace of unreduced cobaltous bromide. For some undiscovered reason, the amount of silver bromide obtained from the residues was still too small to correspond to the weight of the residue if calculated as sodic bromide.

Tests were repeated for sulphuric, phosphoric, and silicic acids with the greatest possible care, but still with negative results. In one analysis the cobalt was determined in the residue and found to be only 0·00013 grm. It is possible, however, that these few tenths of a m.grm. discrepancy are due to the presence of all or at least several of the above-mentioned acids combined with sodium, each in quantity too minute for detection; and for the present this will have to rest as the explanation.

Weight of residue.	Weight of AgBr obtained from residue.	NaBr in residue, calculated from AgBr.	Unidentified.
0·00306	0·00439	0·00240	0·00066
0·00643	0·00978	0·00536	0·00107

SIXTH SERIES.—$CoBr_2$: Co.

No. of analysis.	Sample of $CoBr_2$.	Observed weight of cobaltous bromide in vacuum.	Observed weight of cobalt in vacuum.	Weight of residue.	Corrected weight of cobaltous bromide.	Corrected weight of cobalt.	Atomic weight of cobalt.
		Grms.	Grms	Grm.	Grms.	Grms.	
9.	III.	5·11197	1·38027	0·00306	5·10891	1·37721	59·016
10.	III.	6·41822	1·73333	0·00483	6·41339	1·72850	58·999
11.	III	6·60707	1·78778	0·00902	6·59805	1·77876	59·021
12.	III.	3·03497	0·82249	0·00643	3·02854	0·81606	58·982

Average .. .. 59·004

Average of Series V. and VI. .. .. Co = 58·998

This final average differs from that published before by only about one part in ten thousand; but in comparing the two, one must remember that the material used last year must have been contaminated by the same impurities which have been discussed in this paper. If the impurity contained as much bromine as cobaltous bromide contains, it would have had no effect upon last year's results. In the case of *nickel*, where the impurity consisted wholly of sodic bromide, the effect of correcting the observed results in the paper of 1897 was to raise the atomic weight of nickel from 58·688 to 58·703. The impurity from our *cobaltous* bromide, on the other hand, contained unknown substances in quantities so small as to elude detection, but large enough to change the sign of the corresponding correction. Thus 22·63 grms. of cobaltous bromide in Series V. (the series in which the materials most nearly resembled those used in Series II. and III. of last year's work) were found to contain 0·02327 grm. of impurity. If, as we may reasonably suppose, all the residues obtained from this sample of material resembled that found in Analysis V., Series V., this residue would have yielded 0·0372 grm. of argentic bromide. We may now correct last year's results by subtracting from the several weights of cobaltous bromide proportional weights of impurity, and also subtracting from the several weights of argentic bromide amounts of this substance corresponding to the impurity. Making this correction, the atomic weight of cobalt would be *lowered* 0·008, the averages of Series II. and III. becoming 58·987 and 58·979. Our uncertainty regarding the nature and amount of the impurity thus involves an uncertainty of about one part in six thousand in last year's results. In the light of all the circumstances, it is perhaps safest not to attempt any correction of these values, but to accept them uncorrected as subject to this possible error. The results are accordingly given below in an uncorrected form.

The data just discussed obviously afford a basis for recording the total percentage composition of the cobaltous bromide analysed.

Complete Analysis of Cobaltous Bromide.

(Based upon Series II., III., and V.).

			Per cent.
Cobalt (Series V.)			= 26·923
Total bromine	(II.) 73·050 % (III.) 73·053 % Aver. 73·051 %	= Bromine combined with cobalt	= 72·981
		Bromine actually found in impurity.	= 0·070
Total impurity .. = 0·103 %		= Remainder of impurity (chiefly sodium)	= 0·033
Total			= 100·007

Series VI., perhaps the best of all, is not included in this table, because the material used in it was not quite identical with that used in the three other series. Obviously it is possible to calculate two more ratios involving the atomic weight of cobalt, in which the values for the *bromine* in the bromide are compared with the cobalt found in it. Into this calculation the weight of the bromide itself enters simply as a constant, and an indifferent impurity (such as water) would be eliminated from the result. The table below includes all of the five possible ratios obtainable from our work, Series I. and IV. being rejected because they were merely preliminary:—

2AgBr : $CoBr_2$	(Series II.)	58·995
2Ag : $CoBr_2$	(Series III.)	58·987
$CoBr_2$: Co	(Series V. and VI.) ..	58·998
2AgBr : Co	(Series II. and V.)	58·994
2Ag : Co	(Series III. and V.) ..	58·992
	Average	58·993

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This table, although giving an interesting statement of the possible combinations, does not yield a fair average—for Series V. is introduced three times, Series II. and III. each twice, while Series VI., which is at least as accurate as the others, appears only once. A fairer method would probably be to avoid all hypotheses and combinations, and assign to each of the four series equal weights, as follows:—

Series II. (uncorrected)	.. ..	Co = 58·996
Series III. (uncorrected)	.. ..	Co = 58·987
Series V. (corrected)	.. ..	Co = 58·992
Series VI (corrected)	.. ..	Co = 59·004
Final average	.. ..	58·995

Obviously it makes but little difference which method we adopt; the averages are essentially identical. The highest individual experimental result among all these determinations was 59·021 and the lowest 58·995, the average variation from the mean 58·995 being 0·012. Because these results are less concordant than one could wish, and the conclusion is somewhat less positive than that reached in the case of nickel, the atomic weight of cobalt is being further studied by radically different methods in this Laboratory.

In a recent article (*Zeit. Anorg. Chem.*, xvii., 236), Professor Winkler calls attention to some possible errors in the work upon both nickel and cobalt published last year. That the disagreement between his results and ours is due to the methods employed by him in his work upon these two elements has been sufficiently shown in the preceding paper upon the atomic weight of nickel. In addition, however, his several suggestions concerning our own work should obviously be reviewed and discussed in detail.

His specific criticisms are four in number. First, he suggests that the porcelain tubes might have been attacked during the sublimation of the bromides, with the introduction of foreign bromides into the nickelous and cobaltous bromides. He goes on to state that the bromides were dried in an acid atmosphere, and probably retained hydrobromic acid after this gas had been displaced by air. His third criticism is that the nickelous bromide in the earlier analyses contained nickelous oxide which had to be determined and subtracted; and his final objection applies to the use of the Gooch crucible.

Answers to the greater part of his criticisms can be found in the very articles which he criticises. In one case only can his view be substantiated—the porcelain tubes are really attacked. That this flaw was a possibility we realised at the time; but we also realised the smallness of the error introduced by even a comparatively large amount of such impurity. This matter has been already discussed in detail, both in this paper and in the paper upon the atomic weight of nickel.

There are two possible ways in which hydrobromic acid could have been retained—by absorption and by inclusion. At the high temperatures employed the absorption must have been very slight, and the long process of washing with an indifferent gas was favourable to the elimination of any tendency in that direction. While the inclusion of *liquids* is a very serious possible cause of error, that of *gases* is usually negligible because of the small mass involved. For this reason crystallisation from solutions is far less satisfactory than sublimation as a means of purification.

That as a matter of fact our bromides were neutral there is no lack of evidence. The possibility of acidity had occurred to us also, but reasoning from analogy we had decided that this possibility was rather an improbability. Bromides and chlorides of barium and strontium, heated in the same way in a dry acid atmosphere, after the acid has been displaced by dry air, give absolutely neutral reactions with methyl orange (*Proc. Amer. Acad.*, xxix., 59; xxx., 373). With cobaltous bromide the end point is not as easy to detect as with the before-mentioned halides, on account of the colour of the dissolved salt, but colorimetric comparison makes it possible to distinguish the change very accurately. A solution of our cobaltous bromide containing methyl orange perceptibly changed colour upon the addition of the minimum amount of hundredth normal acid necessary to produce a change of colour in pure water containing methyl orange, showing that the salt must have been very near if not at the turning-point. As a final test, potassium bromide was sublimed in the apparatus which had been used for the preparation of the cobaltous bromide. The sublimate was then heated in a current of dry nitrogen and hydrobromic acid gas, and finally, when cool, the nitrogen and acid were displaced by dry air, just as in preparing the cobaltous bromide for analysis. This potassic bromide upon solution gave an absolutely neutral reaction with methyl orange. Taking into consideration these three points, one cannot believe that enough hydrobromic acid was retained to have had an appreciable influence on our results.

The third critcism, objecting to the fact that in some analyses a small amount of nickelous oxide was found in the bromide, is an unfortunate one. A careful perusal of the work would have shown that only in the preliminary series of results was this the case, and that this series does not enter into the final average, although its results differ only by a very small amount from those subsequently obtained with material free from oxide. As far as the nickel is concerned, a conclusive proof of the absence of acid is afforded by this very fact that the earlier determinations, in which it was necessary to filter off a residue of finely divided nickelous oxide, gave results no higher for nickel than the later results.* Hence the second and the third criticisms are obviously inconsistent with one another.

The advantages of the Gooch crucible are too well known to need mention. Professor Winkler's specific objection to the collecting of displaced asbestos upon an ordinary filter affects only an amount of a few tenths of a m.grm.; and a proof that no error was introduced in this way lies in the fact that in every case the amount of silver bromide found agreed very closely with the amount of silver necessary to complete the reaction, where all but a few tenths of a per cent of the silver was weighed out, and the remainder was added volumetrically. The following brief table will make this clear.

Thus, in the cobalt work, 18·16302 grms. of silver yielded 31·61642 grms. of silver bromide,—a ratio of 57·448 to 100·000,—while in the case of nickel, 15·51556 grms. of bromide gave 26·67078 grms. of silver bromide,—a ratio of 57·444 to 100·000, while Stas found 57·445.

From the cobalt work	AgBr : Ag = 100·000 : 57·448
From the nickel work	AgBr : Ag = 100·000 : 57·444
From Stas's work ..	AgBr : Ag = 100·000 : 57·445

Thus the last of Professor Winkler's criticisms is sufficiently answered.

After necessarily dwelling at such length upon disagreements, it is a pleasure to emphasise other points in which we agree with Professor Winkler. The evidence of our work, together with Dr. Cushman's, strongly supports Winkler's contention that nickel and cobalt, as we know them of old, cannot contain more than an infinitesimal amount of any unknown element. Several radically different methods of preparation and many fractionations invariably led us to constant atomic weights, within a reasonable limit of experimental error; and we are forced to conclude that the familiar properties of these common and useful metals are to be ascribed to elements as definite as any of the seventy-five. It is needless to point out also that we agree with Professor Winkler in assigning to cobalt a higher atomic weight than to nickel, in spite of

* The slight colloidal solubility of nickelous hydroxide was evidently destroyed by the presence of large amounts of nickelous bromide, as one would expect.

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the conflict of periodicity with rhodium and palladium. According to our results, the atom of cobalt, weighing almost exactly 59·00, is very nearly half of 1 per cent heavier than that of nickel.

PROCEEDINGS OF SOCIETIES.

CHEMICAL SOCIETY.

Ordinary Meeting, April 20th, 1899.

Professor Thorpe, F.R.S., President, in the Chair.

(Concluded from p. 212).

55. "*β-Isopropylglutaric Acid.*" By F. H. Howles and Jocelyn F. Thorpe.

β-Isopropylglutaric acid was originally prepared by Schryver, by the reduction of terpenylic acid and synthesised by him in small quantities by the action of ethylic sodiomalonate on ethylic isobutylenemalonate (*Trans.*, 1893, 1345); later, Knoevenagel (*Ber.*, 1898, xxxi., 2585) prepared it by the condensation of isobutaldehyde with ethylic malonate; Schryver's acid melted at 99—100°, Knoevenagel's at 96·5—97°. The authors find that by far the largest yield of this acid is obtained in the following way.

Ethylic β-isopropylacrylate, $Pr^{\beta}\cdot CH{:}CH\cdot CO_2Et$, prepared by eliminating hydrogen bromide from ethylic α-bromisobutylacetate by means of diethylaniline, is a mobile liquid boiling at 174°, which, on condensation with ethylic sodiocyanacetate in alcoholic solution, gives a mixture of a neutral and a hydrogen ethylic salt. Ethylic α-cyano-β-isopropylglutarate, $EtO_2C\cdot C(CN)H\cdot CH(Pr^{\beta})\cdot CH_2\cdot CO_2Et$, is a colourless oil boiling at 195° (30 m.m.), whilst the hydrogen ethylic salt, $HO_2C\cdot C(CN)H\cdot CH(Pr^{\beta})\cdot CH_2\cdot CO_2Et$, is a dark coloured oil which splits off carbon dioxide on distillation and passes into ethylic γ-cyano-β-isopropylbutyrate, $CN\cdot CH_2\cdot CH(Pr^{\beta})\cdot CH_2\cdot CO_2Et$, a mobile liquid boiling at 234°.

The neutral ethylic salt on hydrolysis with methyl alcoholic potash, yields a solid potassium salt, which, on boiling a short time with concentrated hydrochloric acid, becomes the imide,—

$$(Pr^{\beta})CH\begin{matrix}CH_2CO\\CH_2CO\end{matrix}>NH,$$

a solid substance crystallising from water in lustrous plates melting at 120°, and which is quantitatively converted into β-isopropylglutaric acid on boiling for two hours with a 50 per cent solution of sulphuric acid.

β-Isopropylglutaric acid,—

$$HO_2C\cdot CH_2\cdot CH(Pr^{\beta})\cdot CH_2\cdot CO_2H,$$

prepared either in this way or by the direct hydrolysis of the hydrogen ethylic salt with sulphuric acid, crystallises from water in needles melting at 100°, and on treatment with acetyl chloride yields a liquid anhydride boiling at 171° (30 m.m.), and an anilic acid crystallising from dilute alcohol in plates melting at 121°.

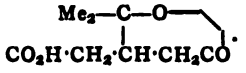
This acid does not appear to be identical with that obtained by Angeli and Rimini (*Gazz. Chim.*, xxvi., 36) from isocamphor on oxidation with potassium permanganate, which melts at 96° and gives an anhydride melting at 60°; further, the dissociation constant K 0·0646 of the authors' acid, as found by Mr. Lidbury, does not agree with K 0·0052 of Angeli and Rimini's acid.

56. "*The Synthesis and Preparation of Terebic and Terpenylic Acids.*" By W. Trevor Lawrence.

The tertiary hydrogen atom in monobasic aliphatic acids is readily oxidised by potassium permanganate (R. Meyer and Fittig).

The author has applied this method to the synthesis of terebic and terpenylic acids.

β-Isopropylglutaric acid is readily oxidised by chromic acid mixture, with the formation of terpenylic acid, confirming Wallach's formula for this acid, namely,—



The synthetic acid is identical with the acid obtained by oxidation of oil of turpentine, melting when anhydrous at 89°, and with 1 mol. H_2O at 56°. It is oxidised by permanganate with formation of terebic acid, and gives the characteristic silver salt, $C_8H_{11}O_4Ag$.

Isopropylsuccinic acid is also easily oxidised by chromic acid mixture to terebic acid, $C_7H_{10}O_4$, which is identical in all respects with the acid obtained by the oxidation of oil of turpentine.

The synthetic acid melts at 175°, and gives the characteristic barium salt of diaterebic acid, $C_7H_{10}O_5Ba,3H_2O$. Under similar conditions, ββ-dimethylglutaric acid remains unchanged.

The yield of the lactone acid is 50 to 60 per cent, the rest being unchanged acid.

Further, it is shown that the separation of terebic and terpenylic acids is easily and completely effected by spreading the mixture of acids on porous plates and heating at 90°; the terebic acid remains as a dry powder on the surface of the plate, and the terpenylic acid is obtained by extracting the plate with water. The author is further engaged in investigating the oxidation products of other similarly constituted acids, and also the action of hydrobromic acid on terebic and terpenylic acids.

57. "*Position-isomerism and Optical Activity: the Comparative Rotatory Powers of Methylic and Ethylic Ditoluylglycerates.*" By Percy Frankland, F.R.S., and Henry Aston.

This forms a continuation of the work on the same subject by P. Frankland, McCrae, and Wharton (*Trans.*, 1896, lxix., 1309, 1583; 1898, lxxiii., 307; 1899, lxxv., 337), the authors having prepared and examined the methylic and ethylic salts of the three isomeric ditoluylglyceric acids. Methylic di-*p*-toluylglycerate (inactive) melts at 98°, the corresponding active salt at 102°; ethylic di-*p*-toluylglycerate melts at 69°; all the other compounds are liquids. The following are the specific rotations:—

Methylic di-*p*-toluylglycerate	..	$[\alpha]_D^{20°}$ = +41·21°
Ethylic ,,	..	,, = +42·41
Methylic di-*m*-toluylglycerate	..	,, = +26·40
Ethylic ,,	..	,, = +26·89
Methylic di-*o*-toluylglycerate	..	,, = +20·19
Ethylic ,,	..	,, = +21·64

The corresponding dibenzoylglycerates, previously prepared by P. Frankland and MacGregor (*Trans.*, 1896, xix., 104) have the following rotations:—

Methylic dibenzoylglycerate (m.p. 58·9°)		$[\alpha]_D^{20°}$ = +26·67°
Ethylic ,,	(m.p. 25°)	,, = +26·08

Thus in this series, again, the *p*-toluyl group has the greatest, and the *o*-toluyl group the least, rotatory effect. The rotatory effect of the benzoyl is almost identical with that of the *m*-toluyl group.

The dextrorotation of all these compounds diminishes with increase of temperature.

The rotatory effects of the isomeric toluyl groups is again found to follow in the same order as that of their molecular volumes, the *p*-toluyl having the largest, and the *o*-toluyl-compounds the smallest, molecular volumes. The molecular volumes of all these compounds are distinctly in excess of the values calculated by means of Traube's formula, and thus afford no evidence of association.

58. "*Fencholenic Acid.*" By G. B. Cockburn, B.A., B.Sc.

The author shows that fenchonoxime, by treatment

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with dilute sulphuric acid, gives, not one nitrile, as Wallach states (*Annalen*, 1891, cclxiii, 136), but a mixture of two isomerides. Of these, one (β) passes easily on saponification to a solid unsaturated acid, $C_9H_{15}CO_2H$, m.p. 72—73°, b.p. 259—260°. The other (α) is very stable, and only gives an acid after long saponification. This acid is isomeric with the former, but is liquid, and boils at 254—256°. Wallach describes the acid he obtained as a liquid, but it is probably a mixture of the above α- and β-acids. The boiling-point of the nitrile, as given by Wallach, is 217—218°, whilst that of the pure β-nitrile re-formed from the pure acid is 211—212°, and of the α- 217—219°. Owing to the difference in behaviour of these two nitriles towards alcoholic potash, the separation of the two acids is comparatively simple.

This behaviour of fenchonoxime bears out the analogy existing between camphor and fenchone. The oximes of both these bodies, by the action of dilute acid, lose a molecule of water in two different ways, and give two isomeric unsaturated nitriles in each case; and these in their turn yield two corresponding acids, one solid, the other liquid.

59. "*The Action of certain Acidic Oxides upon Salts of Hydroxy-acids.*" Part IV. By G. G. Henderson, D.Sc., M.A., T. W. Orr, and R. J. G. Whitehead.

The paper contains the results of investigations carried on in continuation of those formerly communicated to the Society (*Trans.*, 1895, lxvii., 102 and 1030; 1896, lxix., 1451), and a discussion of the constitution of the compounds of the tartar emetic type.

Sodium, *potassium*, and *ammonium molybdicitrates* were prepared by boiling molybdenum trioxide with aqueous solutions of the corresponding primary citrates. They have the formulæ $MoO_2(C_6H_6O_7M')_2,xH_2O$, crystallise in colourless prisms, are readily soluble in water, and are decomposed by heat or light. The barium salt, $MoO_2(C_6H_6O_7)_2Ba,5H_2O$, obtained by precipitation, is a white crystalline powder almost insoluble in water. Decomposed by dilute sulphuric acid it yields a solution which appears to contain molybdicitric acid, $MoO_2(C_6H_7O_7)_2$.

Tungstic oxide, boiled with solutions of mono-alkali citrates, gave *double tungsticitrates* of the formula $WO_2(C_6H_6O_7M')_2,C_6H_7O_7M',xH_2O$; the simple salts are not obtained. These salts form small, colourless crystals, very readily soluble in water, and are not decomposed when heated to 120°. The double barium salt, $2WO_2(C_6H_6O_7)_2Ba$, $(C_6H_7O_7)_2Ba,10H_2O$, prepared by double decomposition, crystallises in minute needles, soluble in water.

Sodium, *potassium*, and *ammonium molybdimalates*, $MoO_2:C_4H_4O_5M')_2,xH_2O$, were prepared like the molybdicitrates. The potassium salt crystallises in large, the sodium salt in small, colourless prisms, and the ammonium salt is a white crystalline powder. All are readily soluble in water, and easily decomposed by exposure to heat or light. Another molybdimalate of sodium, of the formula $MoO_2:C_4H_3O_5Na,1\frac{1}{2}H_2O$, was prepared by heating a solution of monosodium malate with excess of molybdic oxide. It crystallises in long colourless needles, which are soluble in water, is very sensitive to light, and is decomposed by heating to about 90°.

Tungstic oxide is only dissolved with difficulty by solutions of alkali malates, but some *tungstimalates*, $WO_2(C_4H_4O_5M')_2,xH_2O$, were prepared. The sodium salt crystallises in small, the potassium salt in long, needles, the ammonium salt in delicate leaflets. They are readily soluble in water, and can be heated to 105° without decomposition.

With solutions of mono-alkali mucates, molybdic oxide gives in the first instance unstable double salts, $2(MoO_2\cdot C_6H_7O_8M')$, $C_6H_9O_8M',xH_2O$, which are easily soluble in water, and yield the simple *molybdimucates*, $MoO_2:C_6H_7O_8M',xH_2O$. The potassium and ammonium salts are white crystalline powders, fairly easily soluble in water, and decomposed by heating to about 90°. When dry they are fairly stable to light, but their solutions are quickly acted upon.

Potassium tungstimucate, $WO_2:C_6H_7O_8K,3H_2O$, was prepared similarly, but with difficulty. It forms minute lustrous crystals, and is extremely readily soluble in water, and more stable towards heat or light than the molybdimucate.

Potassium molybdilactate, $MoO_2(C_3H_4O_3K)_2$, the only crystalline derivative of lactic acid we have succeeded in preparing, was obtained in the form of small colourless crystals, very readily soluble both in water and in dilute alcohol. It is not very sensitive to light when dry.

Silica was found to be almost insoluble, even when used in the hydrated state, in solutions of all the salts examined.

Sodium, *potassium*, *ammonium titanitartrates*, $TiO(C_4H_4O_6M')_2,xH_2O$, were prepared in the usual way. Hydrated titanic oxide was used, because the anhydrous oxide is practically insoluble in solutions of tartrates. The salts crystallise in small colourless prisms readily soluble in water. Alcohol precipitates from a solution of the ammonium salt a crystalline solid whose composition approximates to the formula $TiO:C_4H_3O_6NH_4$. A white barium salt, almost insoluble in water, is obtained by precipitation.

The corresponding *stannitartrates*,—

$$SnO(C_4H_4O_6M')_2,xH_2O,$$

were prepared similarly. They form small colourless crystals, fairly easily soluble in water. Heating of their solutions in water for any length of time causes slow decomposition of the salts, but in the dry state they are quite stable. From solutions of the potassium and ammonium salts, alcohol precipitates crystalline solids, which appear to have the formula $SnO:C_4H_3O_6M'$. A white barium salt, almost insoluble in water, was also prepared.

Potassium titanicitrate, $TiO(C_6H_6O_7K_2),H_2O$, and *ammonium stannicitrate*, $SnO(C_6H_6O_7NH_4)_2,\frac{1}{2}H_2O$, were obtained by a similar process, though with some trouble. They form small white crystals, very readily soluble in water and soluble in dilute alcohol. They are stable when dry, but gradually decompose if their aqueous solutions are heated.

The hydrated dioxides of titanium and tin were found to dissolve in boiling aqueous solutions of mono-alkali malates, but no definite compounds were isolated.

With some difficulty a *potassium titanimucate*, $TiO:C_6H_7O_8K,3H_2O$, was prepared in the form of small white crystals, easily soluble in water, not sensitive to light, and not decomposed at 100°. No corresponding compound of tin could be obtained.

Collective Index.

Fellows can obtain the Collective Index 1873—1882 from the Assistant Secretary at the price of 10s., or 11s. including carriage. The price of the Collective Index 1883—1892 is 16s. including carriage.

Research Fund.

A meeting of the Research Fund Committee will be held in June. Forms of applications for Grants can now be obtained from the Assistant Secretary.

Silver Sub-oxide.—M. Guntz.—The author has succeeded in proving the existence of sub-oxide of silver, Ag_4O, and preparing the compound by the decomposition of silver oxide, Ag_2O, by heat. Ag_2O begins to decompose slowly at about 250°; at the end of a sufficiently long time the decomposition is complete. After many attempts, the tension of dissociation of Ag_4O was determined.—*Comptes Rendus*, cxxviii., No. 16.

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NOTICES OF BOOKS.

Commercial Organic Analysis. By Alfred Allen, F.I.C., F.C.S. Third Edition. Illustrated. With Revisions and Addenda, by the Author and Henry Leffmann, M.A., M.D. Vol. ii., Part I. London: J. and A. Churchill. 1899. Pp. 387.

The matter dealt with in this volume is the analysis of fixed oils, fats, waxes, glycerol, nitroglycerin, and nitroglycerin explosives; but far the greater part of the book is taken up with oils and fats, their extraction, purification, physical and chemical properties, classification, examination, and identification: there are also given a number of special methods for the examination of fatty oils of all kinds.

The revision has been of a most extensive character, involving every page and almost every paragraph, but, in deference to the author's expressed disapproval of the spelling advised by the American Association for the Advancement of Science, it has not been adopted in this (American) edition, and any instances which may occur are accidental; for this we are thankful.

Some of the most important additions to this volume are:—The bromine thermal method, methods for the determination of glycerol, acetyl number, various tests for the oxidation of oils, composition and official methods for the examination of dynamite and smokeless powders, dégras and cloth oils.

The volume is well and clearly printed, and furnished with a copious index.

Matriculation Directory, No. XXV. The University Tutorial Series. London: W. B. Clive. 1899.

The contents of this book consist principally of old examination papers, and the answers to the questions set. By reading through these the student will get an idea of what sort of questions he will probably have to tackle. This, with articles on the special subjects for June, 1899, and January, 1900, will help him to pass the examination. He will then be ready for more serious study.

Outlines of Industrial Chemistry; a Text-book for Students. By F. H. Thorp, Ph.D., Instructor in Industrial Chemistry in the Massachusetts Institute of Technology. New York: The Macmillan Co. London: Macmillan and Co., Ltd. 1898. Pp. 541.

The wide range of subjects covered by this interesting work prevents any particular process being dealt with exhaustively and completely; the object of the author has, in fact, been to give the outlines of the more important chemical industrial processes, leaving the matters of detail to be acquired by reference to the more comprehensive handbooks and special works.

The author has assuredly succeeded in his endeavour, and has given us a valuable work which cannot fail to be appreciated.

The book is divided into two parts: Part I., on Inorganic Industries, and Part II., on Organic Industries. The first part includes such industries as the manufacture of acids, salt, soda, alkalis, fertilisers, lime, glass, pigments, matches, &c., while Part II. deals with the destructive distillation of wood and bones, the manufacture of illuminating gas, including acetylene and air gas, coal-tar and its derivatives, animal, mineral, and vegetable oils, soaps, resins, starch, sugar, and fermentation industries. The latter covers the wide field of brewing, wine-making, and distilling, also the manufacture of vinegar. Explosives (mainly for industrial purposes) and the textile industries (including fibres, bleaching, mordants, dye-stuffs and dyeing, and textile printing) cover a good number of pages. Paper-making, leather and the tanning industries, and the manufacture of glue, complete the book. A large number of references to Standard Works, Encyclopædias, and Technical Journals are given throughout the text.

The book is well printed and bound, and is furnished with an Index of twelve pages.

The Chemistry of Coke: being the "Grundlagen der Koks-chemie" of O. Simmersbach. Translated and Enlarged by W. Carrick Anderson, M.A., B.Sc. Glasgow and Edinburgh: William Hodge and Co. 1899. Pp. 159.

As the author very truly remarks, it is doubtful whether any extensive manufacture has been less scientific than that of coke; and considering the importance of the subject this is really remarkable,—even the recovery of the by-products is only now beginning to be developed on a large scale.

The manufacture of coke from coal was known and practised in the early part of last century, but its chemical examination only dates back about forty years; certain points had been found by practical experience, but those were known only to a small number of actual workers.

The Introduction of the book deals with the History of the Chemistry of Coke, references being made to the work of Stein, Richters, Muck, Parry, Knublauch, Crace-Calvert, &c. The purpose of coking and the use of coke is described in Chapter I., after which we find the theoretical and practical methods and yields of coking considered, with their influence on the form and appearance of the coke.

Coke is generally regarded only as carbon contaminated with a certain amount of mineral matter; but this view is not correct, as coke may also contain hydrogen, oxygen, nitrogen, and sulphur. The proportions present and the influence of these ingredients is dealt with in the chapter on the chemical composition of coke.

Chapter VII., on the examination of coal and coke, has been added by the translator; it contains methods and details of working which the author has himself found useful in practice.

The book should certainly be found useful to those engaged in the manufacture of coke, and we hope, with the translator, that it will contribute towards placing the industry on a more scientific basis.

Preliminary Report of an Investigation of Rivers and Deep Ground Waters of Ohio, as Sources of Public Water Supply. By The State Board of Health. Cleveland: J. B. Savage Press. 1898. Pp. 259.

This volume contains a series of reports connected with the chemical and bacteriological examination of waters, with a view to deciding whether or no they are suitable for public use. The methods used for carrying out these examinations are to a great extent the same as those used in England, with the exception of those used in the bacteriological examination. We also note that the use of agar is recommended for this work, as the hot summer of Ohio causes the gelatin plate cultures to melt. The reports are very complete, but are naturally only of local interest.

Solubility in Water of Substituted Malonic Acids.—G. Massol and F. Lamouroux.—The solubility of the first five terms of the series of mono-substituted malonic acids have been determined for temperatures between 0° and 50°. The results show that all these acids are very soluble in water, and if their solubilities are represented graphically as functions of the temperature, the curves are straight lines. The introduction of a hydrocarbon radical diminishes the solubility of malonic acid.—*Comptes Rendus*, cxxviii., No. 16.

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CORRESPONDENCE.

SEPARATING TIN OXIDE FROM GANGUE.

To the Editor of the Chemical News.

Sir,—I beg to communicate for your esteemed consideration a method recently employed by me in reference to the separation of tin oxide (present in small quantities) from a siliceous gangue (present in relatively large quantities). As you are well aware such a problem has for years past proved a matter of great difficulty in the satisfactory assay of tin. My method is, briefly, to use Sonstadt's solution, by means of which the felspar and silica may be got rid of at once. With matter in a fine state of division I found vanning unsatisfactory in a high degree as contrasted with this method. The samples I first dealt with contained from six-tenths to two-tenths of a per cent of tin oxide, the gangue mostly siliceous and with a deal of felspar.—I am, &c.,

O. F. Colvin,
Consulting Mining Engineer,
Metallurgist, and Assayer,

21, York St., Moonee Ponds,
Melbourne, Australia,
March 28, 1899.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

Note.—All degrees of temperature are Centigrade unless otherwise expressed.

Comptes Rendus Hebdomadaires des Séances, de l'Académie des Sciences. Vol. cxxviii., No. 16, April 17, 1899.

Heat of Formation and Combustion of some Nitrogen and other Compounds.—M. Berthelot and G. André.—The publication of M. Berthelot's paper on animal heat, suggested the determination of the rate of formation and of combustion of a number of substances found in the animal body and allied nitrogen compounds, which are interesting from a chemical or physiological point of view. Numbers were found for the following substances:—Cholesterine, glycollic and lactic nitriles, xanthine, paraphenylenediamine, nicotine, pyrrol, carbazol; and the indol series—indol, scatol, α-methyl indol, and oxindol. Each of these products was purified with great care and analysed, then the heat of combustion was determined at constant volume.

Solubility in Water of the Normal Acids of the Oxalic Series.—F. Lamouroux.—The author has examined the solubility in water of ten acids of the oxalic series at temperatures between 0° and 65°. The experiments were not continued above this temperature on account of decomposition taking place. The results show that acids with an even number of carbon atoms are relatively less soluble than those with an odd number, and that the solubility decreases rapidly with increased molecular weight. The two first acids, having an odd number of carbon atoms, are very soluble, but those that follow are not more soluble than their homologues of the even groups. Glutaric acid behaves in a peculiar manner; its solubility increases more rapidly than that of malonic acid.

Action of Ethylic, Isobutylic, and Isoamylic Alcohols on their Sodium Derivatives.—M. Guerbet.—Isoamylic alcohol, when heated to 150—160° with its sodium derivative, is partially transformed into diamylic alcohol, $C_{10}H_{22}O$, and isovaleric acid. Isobutylic alcohol scarcely reacts at all on its sodium derivative, even at a temperature of 210—215°; whilst ethylic alcohol, under the same conditions, is partially transformed into ethylene and sodic acetate,—

$$C_2H_6O + C_2H_5NaO = C_2H_4 + C_2H_3NaO_2 + 2H_2.$$

The author proposes to continue this research on alcohols richer in carbon than amylic alcohol.

Bulletin de la Société Chimique de Paris. Series 3, Vol. xxi.-xxii., No. 1.

Absorption of Small Quantities of Carbonic Acid contained in Large Volumes of Gas.—MM. Marboutin, Pecaul, and Bouyssy.—The authors have succeeded in completely absorbing the carbonic acid contained in the air in the Montsouris Park by means of the following arrangement:—The air was made to circulate through an almost horizontal tube, 0·8 metre in length and 11 m.m. in diameter, containing 50 c.c. of a solution of potassic hydrate at 20 grms. per litre; the bubbles of gas joined together and pass through with a speed of about 4 litres per hour, being in contact with the absorbing liquid for at least fifteen to twenty seconds. A second identical tube, placed in continuation of the first, never showed the least trace of carbonation, either with potash or baryta, even after the passage of 200 litres of air. The alkalinity of the second tube was identical with that of the solution used.

Action of Benzoic and Formic Aldehydes on the Ammoniacal Salts.—M. Delépine.—The aromatic aldehydes are capable of giving two orders of isomeric compounds in uniting with ammonia. The first, or hydramides, are decomposed by acids into aldehydes and ammonia; the second are bases belonging to the group of glyoxalidines, not decomposed by acids. The author has shown, after studying the salts of furfurine, that this last property is in perfect accord with the calorimetric results he previously obtained. Thus the equation,—

$$C_{15}H_{12}N_2O_3,HCl \text{ sol.} + HCl \text{ in } 3H_2O = 3C_5H_4O \text{ liq.} + 2NH_4Cl \text{ sol.},$$

which expresses the possible action of hydrochloric acid on furfurine, would absorb 8·5 cals. to be realised. It was only natural to enquire if the inverse action could take place. For this purpose, the author tried benzoic aldehyde; as expected, this aldehyde, when heated with chlorhydrate of ammonia to 180—185°, gives off hydrochloric acid gas and water, while chlorhydrate of amarine, easily separated, is formed.

On Chlorated Hydrobenzamide.—M. Delépine.—Chlorated hydrobenzamide is said to be formed by a loss of HCl when chloride of hydrobenzamide is heated to 180—220°, boiling after several rectifications at 187°. Such a low boiling-point seems incompatible with the formula $C_{21}H_{17}ClN_2$; and, in fact, the author found that the oil formed by the distillation of chloride of hydrobenzamide is only a mixture composed of 2 molecules of benzonitrile and 1 molecule of chloride of benzyl, $C_{21}H_{17}ClN_2 = 2C_6H_5.CN + C_6H_5.CH_2Cl$.

Aromatic Urethanes of Tetrahydroquinolein.—P. Cazeneuve and M. Moreau.—By heating to boiling for two hours 4 molecules of tetrahydroquinolein with 1 molecule of phenolic carbonate, we obtain the phenolic, phenylic orthochlorated, gaïacolic and naphtholic α and β urethanes. Under the same conditions, we have also met with the three cresylic carbonates and carbonate of thymol. By heating tetrahydroquinolein with these carbonates in a sealed tube to above its boiling-point, we should, without doubt, obtain the corresponding urethanes. The authors then go on to describe the methods of preparing and the properties of five urethanes of tetrahydroquinolein they have obtained.

On the Oxazols.—M. Hanriot and G. Reynaud.—When bromoxazolone is treated with warm hydrochloric acid, it easily loses carbonic acid, being transformed into a substituted diethylcetone; only in this case we have a mixture of chlorised and bromised derivatives. A better result is obtained by treating chloroxazolone by hydrochloric acid. If bromoxazolone is dissolved in cold

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potash, the solution hardly becomes yellow, notwithstanding that all the bromine is eliminated in the state of bromide of potassium. The strongly alkaline solution precipitates a viscous matter on the addition of an acid, insoluble in water, soluble in alcohol and ether, decomposing at 30° with evolution of carbonic acid. When bromoxazolone is acted on with hot potash, the principal product is a crystalline mass; this is washed first with water, then with a very little ether, and set to crystallise in a mixture of chloroform and ether. Two kinds of crystals are found; the first melt at 182°, while the mother-liquor contains another body fusible at 137°. By heating bromoxazolone with mercury, a similar result is obtained, but the proportion of the body melting at 137° is higher, while very little of the first lot of crystals fusing at 182° is formed.

Some Derivatives of the Aromatic Metadiamines.—M. Jaubert.—A long paper, not suitable for abstraction.

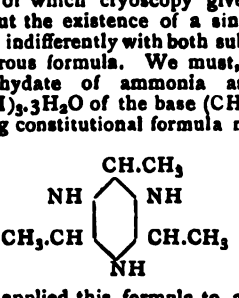
No. 2.

The Reducibility of Metallic Oxides.—H. Hélier.—Already inserted.

On a New Hydrate of the Saline Oxide of Chromium.—G. Baugé.—(See p. 218).

On a New Soluble Antimonic Acid and its Antimoniates.—J. B. Senderens.—By following the instructions given, that is to say, by precipitating the red liquid resulting from the action of nitric acid on trichloride of antimony, with water, we obtain:—1. An antimonic acid, with the formula $Sb_2O_5.nH_2O$, soluble in water. 2. A hydrate, $Sb_2O_5.6H_2O$, produced by the desiccation of the preceding acid freely exposed to the air. 3. The hydrate $Sb_2O_5.3H_2O$, resulting from the desiccation of this latter in the presence of sulphuric acid. 4. Finally, the hydrate $Sb_2O_5.3H_2O$ becomes $Sb_2O_5.2H_2O$, at about 200°; $Sb_2O_5.H_2O$, at about 300°; Sb_2O_5, at about 400°; and this latter gradually changes to Sb_2O_4 when we heat it for a long time to a dull red heat. The author has also prepared a number of antimoniates of nickel, copper, mercury, lead, cadmium, manganese, &c. Many of them, when air-dried, have the formula $Sb_2O_6M.5H_2O$; others contain more water, and resemble the hydrate Sb_2O_5,nH_2O, in which n is greater than 6, and of which the probable existence in solutions of antimonic hydrate has been shown. All these antimoniates, after desiccation in the presence of sulphuric acid, have the general formula $Sb_2O_6M.2H_2O$, corresponding with the antimonic hydrates dried in the same manner, the formula of which is $Sb_2O_5.3H_2O$.

Constitution and Chemical Properties of Ethylidene-imine.—M. Delépine.—The hydrate of ethylidene-imine, as well as the anhydride, have states of polymerisation, of which cryoscopy gives slightly different values; but the existence of a single and unique picrate, obtained indifferently with both substances, points to a single trimerous formula. We must, therefore, consider the aldehydate of ammonia as the hydrate $(CH_3—CH=NH)_3.3H_2O$ of the base $(CH_3—CH=NH)_3$, and the following constitutional formula naturally occurs to one—



The author has applied this formula to a number of experiments, and finds that it not only explains certain known facts, but also adapts itself to new data. These experiments are described at some length.

Action of the *p*-Chlorised and *p*-Bromised Derivatives of Bromomethylphenylcetone on Aniline.—A. Collet.—An alcoholic solution, containing 1 molecule of bromomethyl-*p*-chlorophenylcetone and 2 molecules of aniline, is heated on a water-bath for about a quarter of an hour; on cooling, a yellow crystalline mass separates out; it is but slightly soluble in alcohol, even when warmed. This product is purified by several washings with water to which a little hydrochloric acid has been added, and by crystallisation in a mixture of alcohol and chloroform. In this manner we obtain small bright yellow needles, insoluble in water, slightly so in alcohol, very soluble in chloroform, fusible at about 187—188°, with the composition of a methyl-*p*-chlorophenylcetone anilide, $C_6H_4^{(1)}Cl^{(4)}COCH_2NHC_6H_5$. The action of bromomethyl-*p*-bromophenylcetone on aniline in alcoholic solulution gives an anilide crystallising in pale yellow needles, fusible at 119—120°, insoluble in water, slightly so in alcohol, and very soluble in chloroform.

Methyl-*p*-bromophenylcetone. — A. Collet. — The oxime, $C_6H_4^{(1)}Br^{(4)}C(NOH)CH_3$, was prepared by heating the ketone in alcoholic solution, with an excess of chlorhydrate of hydroxylamine dissolved in a small quantity of water, and previously neutralised with carbonate of soda. It crystallises in alcohol in long colourless needles, slightly soluble in the cold in this solvent, fusible at 128—128·5°. When heated on the water-bath with concentrated sulphuric acid, it is transformed into *p*-bromacetanilide, $C_6H_4^{(1)}Br^{(4)}NHCO.CH_3$, fusible at about 165°.

Methyl-*p*-chlorophenylcetone.—A. Collet.—1 molecule of bromine is added to 1 molecule of methyl-*p*-chlorophenylcetone dissolved in excess of sulphide of carbon or glacial acetic acid; the reaction takes place spontaneously at the ordinary temperature, hydrobromic acid is given off, and the reddish tint of bromine disappears. The solvent deposits crystals fusible at 96°, identical with the product of the action of chloride of bromacetyl on monochlorised benzene in the presence of $AlCl_3$.

The Transformation of the Carbonate of Orthocresol into a Homologue of the Phthalein of Orthocresol. — P. Cazeneuve. — Carbonate of orthocresol, mixed with an excess of soda-lime, heats spontaneously, and undergoes an interesting molecular transposition; it first becomes green and then takes a wine-red colour on the surface through oxidation. The mass, exhausted with water, gives a solution with a fine reddish-violet colour, which is precipitated with HCl, washed, re-dissolved in soda, and re-precipitated. The gelatinous precipitate is dried at a low temperature; it is insoluble in water and benzene, soluble in alcohol, ether, and acetic acid, and will not crystallise.

Action of Phenylhydrazine on Chloranilic Acid.—H. Imbert and A. Descomps.—2·45 grms. of chloranilic acid were dissolved in 150 c.c. of absolute alcohol and poured into 20 c.c. of alcohol containing 2·16 grms. of phenylhydrazine in solution. A very voluminous pearl-grey precipitate is formed, which, under the microscope, shows fine colourless needles. It is washed several times in absolute alcohol, and dried rapidly in vacuo. It gives on analysis C, 50·58; Cl, 16·63; N, 13·87 per cent.

On some Electrolytic Apparatus. — J. Riban. — Several new forms of apparatus are described in this paper, but they cannot be understood without the accompanying diagrams.

The Presence of Di-isopropyl in the Ether of Baku Petroleum. — O. Aschan. — Baku petroleum furnishes, on fractional distillation, a portion boiling at 57—59°, consisting of di-isopropyl, $(CH_3)_2CH.CH(CH_3)_2$. This carbide has been identified with tetramethylethane obtained synthetically by the action of sodium on iodide of isopropyl.—*Ber. der Deut. Chem. Ges.*

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MISCELLANEOUS.

Royal Institution.—A General Monthly Meeting of the Members of the Royal Institution was held on the 8th inst., His Grace the Duke of Northumberland, President, presiding. The following were elected Members:—Mr. A. Cooper, F.R.C.S., Mr. A. W. Porter, Mr. S. Stephenson, and Mr. T. Uzielli. The special thanks of the Members were returned to Mr. Hugh Dewar for his donation of £200, to Mr. Thomas H. Sowerby for his donation of £5 5s., and to Mr. John H. Usmar for his donation of £50 to the Fund for the Promotion of Experimental Research at Low Temperatures. The President referred to the death of Mr. Benjamin Vincent, for many years Assistant Secretary to the Institution, and said that he desired to express the high appreciation that the Managers held of his services.—On Tuesday next, May 16th, Professor W. J. Sollas, F.R.S., will deliver the first of a Course of Three Lectures at the Royal Institution on "Recent Advances in Geology." On Saturday, May 20th, Mr. Edgar F. Jacques will deliver the first of a Course of Three Lectures on "The Music of India and the East, and its Influence on the Music of Europe" (with musical illustrations). And on Thursday, May 25th, Professor L. C. Miall will begin a Course of Two Lectures on "Water Weeds."

New Method for the Preparation of Glycocol.—V. Auger.—Glycocol is generally prepared by Kraut's method, which consists in reacting on monochloracetic acid with a large excess of ammonia, and purifying the product so formed by means of a cupric salt. The author has found it much simpler to react with an alkaline monochloracetate on hexamethyleneamine, molecule for molecule; in such a case it is not necessary to work with dry products. For example, 95 grms. of monochloracetic acid is dissolved in 100 grms. of water, and saturated with a concentrated solution of carbonate of potassium; at the same time add to a solution of commercial formic aldehyde a slight excess of ammonia, and boil to drive off the ammonia. The hexamethyleneamine formed is estimated by evaporating an aliquot part to dryness; mix the two solutions so as to add $1\frac{1}{10}$ molecule of hexamethyleneamine. The temperature rises to about 60°. Evaporate to dryness on a water-bath *in vacuo* for preference. The residue, $(CH_2)_6N_4ClC_2H_2O_2K$, is roughly powdered, and 600 grms. of alcohol at 95° added, and decomposed by the passage of a current of hydrochloric acid gas; formol, chlorides of ammonium and potassium, chlorhydrate of glycocollate of ethyl, and water are formed. The formol is removed by decantation, and the residue washed carefully with alcohol. After distillation, a viscous residue is left; this is diluted with water and boiled with an excess of carbonate of lime and moist oxide of copper. Glycocollate of copper is formed, which is purified and then decomposed by sulphuretted hydrogen.—*Bull. Soc. Chim.*, xxi.-xxii., No. 1.

MEETINGS FOR THE WEEK.

TUESDAY, 16th.—Royal Institution, 3. "Recent Advances in Geology," by Prof. W. J. Sollas, D.Sc., F.R.S.
— Society of Arts, 8. "The Artistic Treatment of Picture Frames," by I. Hunter Donaldson.
WEDNESDAY, 17th.—Society of Arts, 8. "The Law of Trade Marks," by J. E. Evans-Jackson.
— Microscopical, 7.30. Exhibition of Pond Life.
— Institution of Mining and Metallurgy, 8. "The Lucknow (N.S.W.) Goldfield," by A. R. Canning, Assoc.Inst.M.M. "The Silver-Lead Deposits of the Slocan, British Columbia," by J. D. Kendall, M.Inst.M.M. "Notes on the Electro-Deposition of Palladium," by S. O. Cowper-Coles.
THURSDAY, 18th.—Royal Institution, 3. "Embroidery," by Lewis F. Day.
— Chemical, 8. "Corydaline" (Part VI.), by J. J. Dobbie, Ph.D., and A. Lauder. "Oxidation of Furfural by Hydrogen Peroxide," by C. F. Cross, E. J. Bevan, and T. Freiberg.
FRIDAY, 19th.—Royal Institution, 9. "Runic and Ogam Characters and Inscriptions in the British Isles," by The Lord Bishop of Bristol.
SATURDAY, 20th.—Royal Institution, 3. "The Music of India and the East, and its Influence on the Music of Europe" (with Musical Illustrations), by Edgar F. Jacques.

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THE CHEMICAL NEWS.

VOL. LXXIX., No. 2060.

THE THERMAL EXPANSION OF PURE NICKEL AND COBALT.*

By A. E. TUTTON, B.Sc.

THE author has carried out a series of re-determinations of the coefficients of thermal expansion of these two metals with the aid of the interference dilatometer described in a former communication to the Society (*Phil. Trans.*, A, 221, 313; *Roy. Soc. Proc.*, vol. lxiii., p. 208). Since the determinations made by Fizeau in the year 1869, a large amount of additional knowledge has been accumulated with reference to nickel and cobalt, including the discovery of the liquid nickel carbonyl, which places processes of purification in the hands of the chemist of a character so superior to the older methods, as to render it highly desirable that re-determinations of the physical constants of these interesting elements should be carried out with specimens of the metals thus purified. By the kindness of Professor Tilden, who has prepared such specimens with infinite care for the purposes of the investigation of other physical and chemical characters, the author has been enabled to carry out determinations of the thermal expansion with rectangular blocks varying in thickness from 8 to 13 m.m. The blocks were furnished with parallel and truly plane surfaces by the makers of the dilatometer, Messrs. Troughton and Simms. The range of temperature of the observations was from 6° to 121°.

The results of the determinations of the coefficients of linear expansion α are as follows:—

	$\alpha =$	a	$+$	$2bt$
For nickel ..	$\alpha =$	0·000 012 48	+	0·000 000 014 $8t$
For cobalt ..	$\alpha =$	0·000 012 08	+	0·000 000 012 $8t$

Nine different determinations were carried out for each metal, three in each of the three rectangular directions, in order to eliminate any slight error due to directional strain in the metallic blocks. As the metals crystallise in the regular system, the expansion should be the same in all directions. The metal in each case had solidified after fusion in an oxy-hydrogen flame in presence at the last of excess of oxygen. The individual results are highly concordant, the highest result for cobalt being still lower than the lowest of the nine values obtained for nickel. Hence there can be no doubt that the above coefficients represent the true relationships.

The main result of the investigation may be summarised as follows:—The coefficients of linear expansion α of pure nickel and cobalt exhibit a slight but real difference; the coefficient of nickel being distinctly greater than that of cobalt. This is true with respect to both the constant a, the coefficient for 0°, and the increment per degree $2b$, of the general expression for the coefficient at any temperature t, $\alpha = a + 2bt$. The difference is consequently one which augments with the temperature; at 0° it amounts to 3·2 per cent, while at 120°, the upper limit of the temperatures of the observations, it attains 4·5 per cent. Similar rules apply naturally to the cubical coefficients. The metal possessing the slightly lower atomic weight, nickel, is thus found to expand to a greater extent than the metal, cobalt, which is endowed with the higher atomic weight.

* Abstract of a Paper read before the Royal Society, May 4, 1899.

ON THE COMPLEX SALTS OF PLATINUM: OXALATES AND NITRATES.

By M. VÈZES.

IN a previous paper (*Bull. Soc. Chim.*, xiv., 875) I showed that the plato-oxalates $Pt(CO_2CO_2)_2N_2$, and the chloro-platinites $PtCl_4M_2$ (M representing an atom of a monovalent metal), could be brought to the same general type, that of the plato-salts, PtX_4M_2, this relation being shown by the reactions of double decomposition which—the one in neutral solution and the other in acid—allow these two classes of salts to pass from one to the other. An analogous relation exists between the plato-oxalates and the plato-nitrites, $Pt(NO_2)_4M_2$; it is, in fact, possible to pass from one to the other by the reactions of double decomposition.

These reactions, it is true, are in this case more complicated than in the preceding case, on account of the existence of intermediate bodies, possessing great stability and of very easy formation, while no analogous product appears to be formed in the reaction of the passage of the chloro-platinites into plato-oxalates.

I. *Action of Oxalic Acid on Plato-nitrite of Potassium.*—If we pour into a warm concentrated solution of plato-nitrite of potassium a solution of oxalic acid, in such quantity that the mixture will contain a little more than 1 molecule of acid for each molecule of salt, the solution becomes green, and gives rise to a disengagement of nitrous fumes, which can be accelerated by boiling; when this evolution of gas ceases, the solution takes a golden-yellow tint. It is then left to cool, and an abundant deposit of bright yellow crystals is formed, acting on polarised light. The salt thus obtained has the formula $Pt(CO_2.CO_2)(NO_2)_2K_2 + H_2O$, and was formed under these conditions by a regular exchange reaction:—

$$Pt(NO_2)_4K_2 + CO_2H.CO_2H = Pt(CO_2.CO_2(NO_2)_2K_2 + 2NO_2H.$$

This salt, to which we will give the name plato-oxalo-nitrite of potassium, is thus a substitution product of the plato-nitrite, in which two groups $X = NO_2$, derived from the nitrous acid NO_2H, are replaced by the divalent radical $X_2 = CO_2.CO_2$, derived from the oxalic acid, $CO_2H.CO_2H$. In its constitution it corresponds to the mixed chloro-nitrated, bromo-nitrated, and iodo-nitrated salts, also very stable in aqueous solution, which I have already described (*Ann. Chim. Phys.*, Series 6, xxix., 145), obtained by the regulated action of hydrochloric, hydrobromic, and hydriodic acids on plato-nitrite of potassium, viz., the plato-dichloronitrate, $PtCl_2(NO_2)_2K_2$, the plato-dibromonitrite, $PtBr_2(NO_2)_2K_2$, and the plato-diiodo-nitrite, $PtI_2(NO_2)_2K_2$; this latter has been already obtained by Nilson (*Journ. f. Prakt. Chim.*, Series 2, xxi., 172) by a different method. The reaction of oxalic acid is similar to that of the hydracids, with this difference—that, in view of its bibasicity, a single molecule of acid instead of two takes part in the reaction.

If in this reaction we use a less quantity of oxalic acid than that mentioned above, we still obtain the same salt; but the mother-liquor from the crystallisation, concentrated in its turn, deposits a part of the plato-nitrite unchanged. Thus, under these conditions, it does not form the stable salt with the composition intermediate between that of the plato-nitrite and of the plato-oxalonitrite, and which corresponds to the plato-monochloronitrite $PtCl(NO_2)_3K_2$, and to the plato-monobromonitrite, $PtBr(NO_2)_3K_2$, already described (*loc. cit.*, pp. 178 and 194). The use of an excess of oxalic acid not only prevents the formation of any other mixed salt besides the plato-oxalonitrite, but it also effects the alteration of the appearance of the product obtained. Its colour becomes deeper, passes to brownish-yellow, and then to yellowish-green, without any appreciable change in its composition. The analysis of this green salt, which will be published later on, shows, in fact, that it still possesses, with the

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exception of a slight excess of carbon and a very slight deficit of nitrogen, the composition of the plato-oxalonitrite: from this we may conclude that it consists of plato-oxalonitrite, modified in its appearance by its mixture with a little plato-oxalate.

Now, if we act on the plato-nitrite with a large excess of oxalic acid, and if we prolong the action of heat on the mixture, we observe that the liquid becomes brown, and gives, on cooling, simultaneously with this green salt, very fine copper-red needles of plato-oxalate of potassium, $Pt(CO_2.CO_2)_2K_2+2H_2O$, resulting from the exchange reaction—

$$Pt(NO_2)_4K_2+2CO_2H.CO_2H = Pt(CO_2.CO_2)_2K_2+4NO_2H,$$

and corresponding perfectly with the description given by Söderbaum ("Studier öfver Plato-oxalyl föreningar," p. 21; *Thèse Upsal*, 1888) of the deep-coloured isomer of this salt (*Bull. Soc. Chim.*, xix., 876). From this we see, as we should expect, that the plato-oxalate constitutes the final phase of the reaction of oxalic acid on the plato-nitrite. But the elimination of the nitrous acid is difficult to complete, and we always obtain, at the same time as these copper-red needles, greenish crystals of the impure plato-oxalonitrite mentioned above. The separation of these two salts, both only slightly soluble in the cold, is very difficult; at the most we can, by fractional crystallisations in supersaturated solutions, obtain mixtures rich in one or the other of the two salts. From this it results that the reaction just described, although it gives evidence of the relations existing between the plato-nitrites and the plato-oxalates, does not constitute a convenient method for the preparation of the dark coloured plato-oxalate of potassium.

II. *Action of Nitrite of Potassium on Plato-oxalate of Potassium.*—Söderbaum (*loc. cit.*, p. 78; and *Berichte*, xxi., 267, ref. 1888) observed that an excess of nitrite of potassium added to a warm solution of the dark plato-oxalate of potassium, takes away the colour, and on cooling gives a deposit of plato-nitrite. The passage of the plato-oxalate into plato-nitrite is thus effected in neutral solution by the reaction—

$$Pt(CO_2.CO_2)_2K_2+4NO_2K = Pt(NO_2)_4K_2+2CO_2K.CO_2K.$$

I have confirmed this result, but I can further state that it is possible, by using moderate and progressive quantities of nitrite of potassium, to pass, in the inverse order, through all the intermediate stages described in the preceding paragraph; we obtain, in fact, successively the above-mentioned green salt, then the normal plato-oxalonitrite, and finally the plato-nitrite, which is the final phase of the reaction.

Again, while Söderbaum states that the dark plato-oxalate alone is susceptible of the transformation, and that nitrite of potassium is without action on the solution of the pale plato-oxalate, I have observed, on the contrary, that nitrite of potassium acts equally on one and the other of these two isomers. Below, for example, are some analytical data relative to the colourless crystalline product obtained by the action of an excess of nitrite of potassium on the pale plato-oxalate of potassium:—

1. 0·4966 grm. of material, dried in the cold, and not losing any weight after heating for twenty-four hours to 110—120°, was carried to a dull red heat, and under these conditions gave off an abundance of nitrous fumes, and left a residue weighing 0·4289 grm., appearing to consist of platinum and nitrate of potassium: this residue, heated to redness with an excess of sulphuric acid, gave 0·2130 grm. of platinum and 0·1866 grm. of sulphate of potassium, containing 0·0838 grm. of potassium.

2. 0·8678 grm. of the same material, heated to redness with an excess of tungstic acid, gave (after the passage of the gases through heated tubes of copper and oxide of copper) 83·9 c.c. of nitrogen at 0° and 760 m.m. weighing 0·1052 grm.

	Calculated.		Found.	
Pt	194·8	42·60	42·89	—
2K	78·2	17·10	16·88	—
4N	56·2	12·29	—	12·12
8O	128·0	28·01	—	—
$Pt(NO_2)_4K_2$	457·2	100·00	—	—
$Pt+2NO_2K$	369·1	80·71	80·47	—
$Pt+SO_4K_2$	397·1	86·86	86·37	—

The pale plato-oxalate of potassium is thus, like the corresponding dark salt, transformable into plato-nitrite by the action of an excess of nitrite of potassium, with this difference, that, even when using a very small quantity of the reagent, we never obtain with the pale plato-oxalate the green salt mentioned above; the only phase of the transition is in this case the normal plato-oxalonitrite. The error here committed by Söderbaum is easy to explain: this plato-oxalonitrite having the same pale yellow colour as the pale plato-oxalate, and being, in a superficial examination, easily mistaken for it. As for the absence of the greenish salt among the products of this reaction, it appears to be explained by the neutrality of the solution; that is a point to which I shall return, as its study appears to lead to the true interpretation of the isomerism of the plato-oxalates.

It should be remarked that the impossibility of obtaining, in the above-mentioned reaction, any other stable salt with a composition intermediate between the plato-nitrite and the plato-oxalate, except the normal plato-oxalonitrite or its greenish modification, again points to the remarkable stability shown amongst the mixed plato-salts by the compounds of the form $PtX_2Y_2K_2$, a fact pointed out in my previous research (*Ann. Chim. Phys.*, Series 6, vol. xxix., pp. 181, 193, 197, 206), and which Miolati has recently confirmed (*Rendiconti della R. Acad. dei Lincei*, 1896, vol. ii., p. 144).

III. *Other Methods of producing Plato-oxalonitrite of Potassium.*—The relations existing between the plato-oxalates and the plato-nitrites, and notably that which results from the existence of an intermediate plato-oxalonitrite, can be seen by other reactions in which the same salt is formed. It can, in fact, be obtained by the mixture of equal quantities of solutions of the plato-nitrite and the plato-oxalate, the pale variety of this latter salt thus giving rise to the normal oxalonitrite, the dark isomer giving, on the contrary, the greenish salt of almost identical composition.

Further, it is easy to predict, and experiment confirms the fact, that the chloro-, bromo-, and iodo nitrated salts of platinum, of the form $PtX_2Y_2K_2$, will give the oxalonitrite by the same reaction which enables the chlorised, bromised, and iodised salts to pass to the state of oxalate. In this way the action of an excess of neutral oxalate of potassium on the plato-dichloronitrite of potassium, $PtCl_2(NO_2)_2K_2$, gives the normal plato-oxalonitrite—

$$PtCl_2(NO_2)_2K_2+CO_2K.CO_2K = Pt(CO_2.CO_2)(NO_2)_2K_2+2KCl.$$

The inverse passage of the plato-oxalonitrite to the plato-dichloronitrite is also caused just as easily by double decomposition with a metallic chloride capable of forming an insoluble oxalate. In this way the action of the chlorides of calcium, lead, and copper give, with the deposition of the metal in question, a yellow liquor, giving after concentration crystals of plato-dichloronitrite of potassium. We have, for example, in the case of chloride of calcium—

$$Pt(CO_2.CO_2)(NO_2)_2K_2+CaCl_2 = PtCl_2(NO_2)_2K_2+C_2O_4Ca.$$

In the same manner the plato-dibromonitrite and the plato-diiodonitrite have been obtained from the plato-oxalonitrite, one by means of bromide of magnesium, and the other with iodide of lead.

These reactions show that the groups CO_2 of the oxalonitrite play in this body the same *rôle* as the atoms of chlorine, bromine, and iodine in the above mixed salts, and also help to show the analogy of constitution existing

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between these three classes of complex salts of platinum—the oxalates, the chlorides, and the nitrites.—*Bull. Soc. Chim.*, Series 3, vol. xxi., No, 4.

ON THE

CHEMICAL REACTIONS INVOLVED IN THE AMALGAMATION OF SILVER ORES.*

By H. F. COLLINS, M. Inst. M.M.

THE experiments of Laur, Huntington, and others have proved that the principal reagents in the patio process are mercury and cuprous chloride.

Most metallurgists appear to have taken it for granted that, as regards the chloride of copper at all events, the reactions taking place in the pan are similar to those of the patio process, and the conclusions of Hague, based on his own experiments, have been accepted without question.

The functions of the iron of the pan itself, together with that existing in the pulp in a finely divided condition, to the amount of 3 to 10 lbs. per ton of ore, and resulting from the abrasion of battery and pan castings, are summed up by both Hague and Egleston as follows:—(1) Direct reduction of AgCl to metal; (2) Reduction of calomel; (3) Direct reduction of Ag_2S; and (4) Reduction of $CuCl_2$ to Cu_2Cl_2; and both agree that the mercury and iron aided by heat and friction are the principal reagents in the extraction of the precious metals in the Washoe process. In the author's opinion, the part played by bluestone in the pan has been very generally misunderstood; the formation of Cu_2Cl_2 can only be accidental and momentary, and all the copper added is reduced to metal almost as soon as it is dissolved. It is indeed well known that practically all the copper added to a pan charge is eventually taken up by the mercury; it does not, however, seem to have occurred to any one to trace the stage at which the copper becomes amalgamated, or to doubt that Cu_2Cl_2 is formed by the action of even a large excess of iron upon $CuCl_2$.

The classical experiment of Hague, upon which so much misconception of the action of copper sulphate has been based, was as follows:—

Two grms. of powdered blende, 1 grm. iron filings, 5 grms. NaCl, 7 grms. $CuSO_45Aq$, were placed in a flask with a little water and kept at 90° C. for a few days. The iron filings rapidly disappeared; metallic copper was precipitated, but re-dissolved probably by the chloride of copper present, the subchloride being formed. Later the iron was thrown down as a basic salt by absorption of atmospheric oxygen. It would appear that Hague, and those who followed him, inferred from this that the Cu_2Cl_2 is formed during amalgamation; but under the existing conditions there are three equivalents of copper present for two of iron, so that there is not sufficient iron present to precipitate the copper, which would require equal equivalents. In investigating the subject the author made the following experiments:—

1. Repeated Hague's experiment in triplicate, leaving out the blende, and, instead of standing for some days, boiled for fifteen minutes, thirty minutes, and two hours respectively, then determined the dissolved copper. The amounts of copper remaining undissolved were respectively 55, 24, and 12·5 per cent of the total amount present.

2. In the presence of free metallic iron in excess, $CuCl_2$ dissolved in excess of NaCl was rapidly reduced to the metallic state. It appears, therefore, that Cu_2Cl_2 in the pan-charge would be almost instantaneously reduced by the large excess of iron present.

3 and 4. A measured quantity of a copper-salt solution was ground with sand in an iron mortar for periods of five and ten minutes. After five minutes' grinding only 6 per cent of the total copper was found to be still soluble in water, and after ten minutes' grinding only 2 per cent, the whole of the remainder having been precipitated. The supposed existence of cuprous chloride in pan pulp is therefore a myth, and the active reagent introduced by the addition of bluestone to the pan-charge is finely divided metallic copper, which soon becomes amalgamated, without, however, losing its power of acting on silver compounds.

A series of experiments was next undertaken with a view to ascertain the relative activities of iron, copper, mercury, and cuprous chloride, in liberating silver from its compounds. In order that the experiments might be made under similar conditions, a shaking frame was prepared to hold six stoppered bottles, into which the silver compounds and the reagents were put.

5. To equal quantities of freshly precipitated AgCl with excess of salt were added equal equivalents of the following substances, and after ten minutes' agitation the excess of AgCl was dissolved in ammonia, and the precipitated silver determined. The results were as follows:—

Reagent added.	Per cent of total Ag precipitated.
1 equivalent of Hg	12·56
1 ,, iron filings ..	28·80
1 ,, copper precipitate	88·50
1 each copper sulphate and iron filings	97·10

As the much more rapid effect of the precipitated copper was judged to be due to its more finely divided state, another experiment (No. 6) was made, by which, to equal weights of freshly precipitated AgCl in excess of salt, equal surfaces of the three metals were exposed for equal times at a boiling temperature. The results were as follows:—

Metallic surface.	Per cent of Ag precipitated.
Mercury	13·2
Sheet iron	91·9
Sheet copper	93·3

These experiments throw light on the well-known fact that docile chloride ores can be treated better, and with less loss of mercury in the iron pan, than in the patio. The results on sulphide ores are, however, known to be different, and the next series of experiments on an artificial mixture of sand and silver sulphide was made to investigate this difference.

7. Silver sulphide was ground with excess of sand, mercury, salt, and the following special reagents in a Wedgwood mortar, and the silver, reduced to the metallic state, determined by taking up with mercury, panning off, and retorting. The mean results of eight sets of experiments were as follows.—

Special reagent added.	Per cent of Ag reduced to metal.
Iron filings	2·60
Precipitated copper ..	5·99
Cuprous chloride	7·62
Cu_2Cl_2 and iron filings ..	10·66
$CuSO_4$ and iron filings ..	3·20
None	2·00

The above experiments not seeming to point to any definite conclusion beyond proving that cuprous chloride has a more powerful effect than metallic copper or iron, another set of experiments was made in bottles contained in the shaking frame.

8. To equal quantities of silver sulphide were added excess of mercury and salt, and the special reagents mentioned below. The total time of contact was eighty hours, of which twenty-six hours was at the boiling temperature with constant agitation. The results were:—

* Abridged from a Paper read before the Institution of Mining and Metallurgy, April 19th, 1899.

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Special reagent added.	Per cent of Ag reduced to metal.
Iron filings	32·8
Copper precipitate (fresh)	37·0
Cu_2Cl_2 and copper filings	72·3

This experiment confirms the former, and shows clearly that the effect of metallic copper upon Ag_2S, though more powerful than that of iron, is less powerful than that of Cu_2Cl_2. This explains the rooted aversion which patio and fondo amalgamators have to the use of iron in grinding unless counterbalanced by a comparative enormous subsequent excess of bluestone, and the undoubted fact that on raw sulphide ores the patio or fondo will extract a better percentage than the pan in which the addition of bluestone, in even large amount, can only result in the formation of metallic copper, but, as already shown, never in that of the more active Cu_2Cl_2.

The conclusions which may be drawn from a consideration of the above experiments are the following:—

1. When treating "chloride" silver ores, the iron pan will give at least as perfect an extraction as the patio, with far less loss of mercury, owing to the fact that the affinity of iron for the chlorine combined with the silver is so much greater than that of mercury (Expts. 5 and 6).

2. When treating such ores in the pan, the reactions are not sufficiently accelerated by the use of bluestone to compensate for the increased cost. Similarly, the increase in rapidity by the substitution of the copper fondo for the iron pan does not justify the increased cost (Expt. 6).

3. When treating sulphide ores, however, the extraction is much accelerated and increased by the addition of bluestone (Expts. 7 and 8).

4. The bluestone, when added to the pan-charge, is very speedily reduced to metal. The copper so precipitated amalgamates with the mercury, and acts upon silver sulphide more energetically than either metallic iron or mercury, or both combined (Expts. 7 and 8). No cuprous chloride is formed in the pan, or, if formed temporarily by the secondary action of precipitated copper upon undecomposed cupric chloride, it is reduced to metal by the excess of iron present, long before it can exercise any effect upon the silver sulphide present (Expts. 1 to 4).

5. That nevertheless cuprous chloride has a still more powerful effect upon Ag_2S than metallic copper, however freshly precipitated (Expts. 7 and 8).

6. That this powerful effect of Cu_2Cl_2 explains the observed fact that upon raw or badly roasted sulphide ores, the fondo (in which Cu_2Cl_2 is constantly regenerated for re-use, gives a better extraction than the pan (in which Cu_2Cl_2, if accidentally formed, is almost at once decomposed).

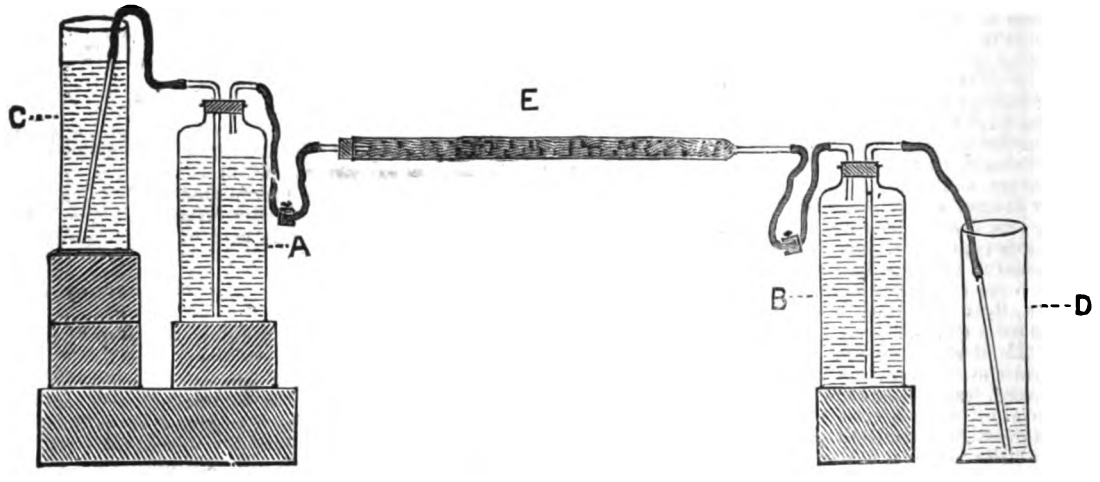
Anticipating criticism of these experiments as unpractical on the ground that they refer to processes which are either obsolete or rapidly becoming so, the author thinks it well to recall the fact that over one-fourth of the world's total output of silver is still produced by amalgamation processes, which in countries where the ores and conditions are suitable—as in parts of Mexico, Columbia, Bolivia, and Peru—are likely to hold their own as against smelting processes for at least another century to come.

LABORATORY NOTES.

By W. FRENCH and J. M. BROTHERS.

Volume Composition of Carbon Monoxide.

The accompanying sketch will explain a method used here for class work, and which has given satisfactory results. A and B are two syphon bottles with the syphon-tubes dipping into C and D respectively by rubber and glass tubing. The liquid in the four vessels is water previously saturated with carbon dioxide gas. Carbon dioxide is passed into A until it is about one-third full; it is then connected to the combustion-tube E, containing



scrap charcoal (recently ignited), and the air replaced by CO_2 from A. B, which is quite filled with CO_2 water, is now connected to the other end of E, the syphon-tube filled and dipped into D. The tube E (about 2 feet long) is now heated in a combustion furnace; when the charcoal is red-hot, A and C are raised whilst B and D are lowered (C being higher than A, and D being lower than B), the gas slowly passing from A to B; when all the gas has passed over to B, the levels of the bottles are reversed and the gas is passed back to A.

The process is repeated about four times and cooled. The volume is then found to have been doubled, and readily proved to be carbon monoxide. The same apparatus, having copper in the tube E, is also used to determine the volume composition of the oxides of nitrogen. Three or four students working together may easily perform the experiment, and it possesses advantages over the use of mercury and sodium for elementary students.

Bury Grammar School.

Physical Society.—Owing to the resignation of Mr. Appleyard, Mr. R. W. Forsyth has been appointed Reporter to the Physical Society of London.

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THE CONSTITUTION OF THE AMMONIUM-MAGNESIUM PHOSPHATE OF ANALYSIS.*

By F. A. GOOCH and MARTHA AUSTIN.

In a recent paper from this laboratory (*Am. Journ. Sci.*, vi., 233) it has been shown that the presence of ammonium chloride or other ammonium salt is necessary in the precipitation of manganese as the ammonium-manganese phosphate by microcosmic salt in order that the precipitate may have the ideal constitution represented by the symbol NH_4MnPO_4.

It was also shown that the solvent effect of the ammonium chloride upon the precipitated ammonium-manganese phosphate is not marked when an excess of the precipitant is present in solution.

The relations disclosed in this paper suggest that the chemical constitution of the precipitate rather than mechanical contamination and varying solubility—the explanations generally accepted, and, indeed, advocated by one of us in a former paper (*Am. Chem. Journ.*, i., 391)—may be responsible for observed variations in the weight of the residue derived by the ignition of the similar salt of magnesium, the ammonium-magnesium phosphate, precipitated by an excess of a soluble phosphate from the solution of a magnesium salt, or from the solution of a soluble phosphate by an excess of a magnesium salt.

Precipitation by Excess of the Soluble Phosphate.

The precipitation of the magnesium salt by an excess of the soluble phosphate was first studied. For this work a solution of pure magnesium nitrate was prepared by dissolving the pure magnesium oxide of commerce in a slight excess of pure hydrochloric acid and boiling with more magnesium oxide. After filtering off the excess of magnesium oxide and any trace of iron or members of the higher groups, the solution was precipitated by ammonium carbonate, the precipitate was washed by repeated boilings and filtrations until silver nitrate gave no precipitate in the solution acidified with nitric acid. This precipitated carbonate was nearly dissolved in nitric acid, and the solution was boiled with an excess of the carbonate (for the purpose of removing traces of barium, strontium, and calcium), filtered, and diluted to definite volume. The evaporation of a definite volume of the solution and strong ignition of the residue would be a most natural method of establishing a standard of the solution, were it not for the fact pointed out by Richards and Rogers (*Am. Chem. Journ.*, xvi., 567) that the oxide of magnesium retains on ignition occluded nitrogen and oxygen enough to increase its weight sensibly. For this reason the nitrate was converted to the sulphate and weighed as such—either by evaporating to dryness in a weighed platinum crucible a definite volume of the solution, igniting as oxide, and changing to the sulphate by heating with sulphuric acid; or, by evaporating the magnesium nitrate directly with an excess of sulphuric acid of half strength. In this treatment the excess of acid was removed by heating the platinum crucible upon a porcelain ring or triangle so placed within a porcelain crucible that the bottom and walls of the inner crucible were distant about 1 c.m. from the bottom and walls of the outer crucible. The excess of acid is easily removed in this way, and the outer crucible may be heated to redness without danger of breaking up the magnesium sulphate. The results of this work, taking O = 16, Mg = 24·3, N = 14·03, S = 32·06, are given in the accompanying table.

The magnesium oxide obtained by direct ignition of the nitrate weighed on the average about 0·0010 grm. more than the oxide theoretically present in the weighed sulphate from equal portions of the solution.

Table I.

$MgSO_4$ obtained by converting ignited MgO into the sulphate.	$MgSO_4$ obtained directly from 50 c.m.³ $Mg(NO_3)_2$.	Theoretical amount of MgO in $MgSO_4$.
Grm.	Grm.	Grm.
0·5748	—	0·1924
0·5739	—	0·1923
—	0·5741	0·1922
—	0·5750	0·1925

Before proceeding to study possible chemical effects of ammonium chloride in determining the constitution of the ammonium-magnesium phosphate, it is obviously necessary to define the extent to which the ammonium salt may exert a solvent action in presence of the precipitant. Fresenius estimated that ammonium-magnesium phosphate is soluble in 15,293 parts of cold water, but the method of investigation employed did not entirely preclude the possibility of counting as ammonium-magnesium phosphate soluble material included and held in the original precipitate ("Fresenius," 6te Aufl., p. 805). According to Kissel (*Zeit. Anal. Chemie*, viii., 173), the phosphate, which dissolves in a mixture of ammonia and water in the proportion of 0·0040 grm. to the litre and in the proportion of 0·0110 grm. to the litre in a similar mixture containing also 18 grms. of ammonium chloride, is practically insoluble in the latter mixture if an excess of magnesia mixture be added; and Heintz (*Zeit. Anal. Chemie*, ix., 16) showed that the effect of adding an excess of sodium phosphate in the solution is similar.

So far as appears, no quantitative experiments have been recorded in which the behaviour of a mixture of ammonium chloride and magnesium salt and an insoluble phosphate in a solution only slightly ammoniacal has been tested, though as a matter of convenience the use of faintly ammoniacal solutions and faintly ammoniacal wash-water is to be preferred to the mixture of strong ammonia and water (1 : 3) ordinarily employed. As a preliminary step, therefore, in the work to be described, experiments were made to find how small an amount of magnesium could be detected in solution by precipitating with microcosmic salt, either alone or in presence of ammonium chloride in faintly ammoniacal solutions. The ammonium chloride used for these tests (as well as in the similar quantitative work following) was purified by boiling with a faint excess of ammonia, filtering, digesting twelve hours with microcosmic salt, and filtering again. The results are given in Table II.

Table II.

Weight of MgO taken as the nitrate. Grm.	$H(NH_4)NaPO_4 4H_2O$ taken. Grms.	Volume. C.m.³.	NH_4Cl taken. Grms.	Opalescent precipitation.
0·0003	1·75	100	—	Marked.
0·0003	1·75	500	—	,,
0·0003	1·75	100	10	,,
0·0003	1·75	500	10	,,
0·0003	1·75	500	30	Faint.
0·0001	1·75	100	—	Marked.
0·0001	1·75	100	10	,,
0·0001	1·75	500	10	Faint.
0·0001	1·75	500	60	,,

The results of these tests show that even so little as 0·0001 grm. of magnesium oxide may be detected in 500 c.c. of faintly ammoniacal water containing as much as 60 grms. of ammonium chloride.* It is plain that strongly ammoniacal liquids are entirely unnecessary in the precipitation of the ammonium-magnesium phosphate under the conditions. In nearly all the experiments to be detailed use was made, therefore, of faintly ammoniacal solutions and wash-water.

(To be continued).

* Contributions from the Kent Chemical Laboratory of Yale University. From the *American Journal of Science*, Series 4, vol. vii., No. 39, March, 1899.

* It was found also, incidentally, that the presence of reasonable amounts of ammonium oxalate (100 c.m.³ of the saturated solution) does not interfere with the precipitation of the ammonium-magnesium phosphate by microcosmic salt.

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PROCEEDINGS OF SOCIETIES.

CHEMICAL SOCIETY.

Ordinary Meeting, May 4th, 1899.

Professor THORPE, F.R.S., President, in the Chair.

MESSRS. David Hooper and W. H. Mills were formally admitted Fellows of the Society.

Certificates were read for the first time in favour of Messrs. Henry Meldola Danziger, Clent House, Woodland Road, Northfield, Birmingham; William Gordon Fraser, Golspie, St. Albans; Henry Royal-Dawson, 3, Kenilworth Road, Ealing, London, W.; Samuel Stansfield, White Lee, Mytholmroyd, Manchester; Christopher Joseph Whittaker, Willow House, Blackburn Road, Accrington.

A ballot for the election of Fellows was held, and the following were subsequently declared duly elected:—

James Herbert Allworthy, Peter Auchinachie, Clement Harrison Baker, Frederick James Beale, Frank Belton, Benjamin Harvey Bennetts, Alfred Ernest Bond, George Smith Bratby, Kendall Colin Browning, B.A., William Collingridge, M.A., Robert D. Connell, Charles Robert Darling, Harold Francis Carl Goltz, Percy Haigh, John Elias Hughes, Archibald Glen Kidston Hunter, Lauder William Jones, B.A., Ph.D., Thomas Judge, B.A., Robert William Lindsey, James MacLeod, William McConnell, Wilfred Walter Morris, Laurence C. Panting, B.A., M.B., Frederick Williams Pittuck, Harold McLean Read, S. B. Schryver, D.Sc., Ph.D., Maurice Emile Schweich, Edward Thomas Shelbourn, Arthur John Shelton, Harry Alexander Thiersch, Robert Tatlock Thomson, Richard Threlfall, Ernest Albert Tyler, B.A., Arthur Luvian Wade, Allan Frederick Walden, M.A., Charles Walker, Fred Sheasby Watson, B.Sc.

Of the following papers those marked * were read:—

*60. "*On the Combustion of Carbon Disulphide.*" By HAROLD B. DIXON and E. J. RUSSELL.

The authors have investigated the temperature of ignition of carbon disulphide in air, its stability on heating, its mode of burning in air in the divided flame, and its explosion with oxygen.

Experiments on the ignition point of carbon disulphide showed considerable variations. It was found that the vapour undergoes a phosphorescent combustion in air similar to that of phosphorus, sulphur, ether, &c. This phosphorescence is well seen in a dark room when the vapour impinges on a glass vessel at 230°. The lowest temperature at which actual ignition was observed was 232°. Carbon disulphide distilled in a current of nitrogen through a porcelain tube heated to 400° showed no visible decomposition. When carbon disulphide was sealed up in a glass tube and submitted to prolonged heating at 230°, a slight yellow film formed on the glass. A similar film was produced by the prolonged action of bright light.

Although carbon disulphide is decomposed by a violent shock (*e.g.*, an explosion of fulminate) into its elements, this decomposition is not propagated through its vapour as an explosion, but dies out. When carbon disulphide is exploded with defect of oxygen, it does not yield a deposit of carbon. When it is exploded in a long tube with an excess of oxygen, the products of the combustion are mainly those required by the equation $CS_2+3O_2=CO_2+2SO_2$, but there are always present small quantities of carbon disulphide, oxysulphide, and monoxide with the excess of oxygen.

When carbon disulphide is exploded in a long tube with insufficient oxygen for complete combustion, the products are carbon dioxide and sulphur dioxide along with carbon oxysulphide and monoxide, sulphur, and unchanged carbon disulphide. As the oxygen is gradually diminished, the amount of sulphur dioxide falls off, whilst the carbon monoxide increases. The authors were unable to set up the explosion-wave in mixtures containing less than 40 per cent of oxygen. So far as the experiments could be carried, there was always a division of the oxygen between the carbon and sulphur. No simple equation expresses the mode of burning. In the incomplete combustion of carbon disulphide, the sulphur was deposited partly in the "liquid" condition.

The maximum velocity of the explosion-wave was found when the oxygen just sufficed for complete combustion.

When carbon disulphide vapour and air are burnt as the Smithells divided flame, the products of the inner flame are sulphur dioxide and carbon monoxide in nearly equal volumes, some unchanged carbon disulphide, and only small quantities of carbon dioxide and oxysulphide.

DISCUSSION.

Professor TILDEN said that it seemed to him impossible to determine or to state exactly the temperature of ignition of any combustible substance, inasmuch as this depends largely upon conditions such as the proportion of air present, and especially the extent of the heated surface by which the action is started. As an example, the very small, though very hot, sparks from a flint and steel are known to be incapable of inflaming a mixture of coal-gas and air, while a red-hot iron-bar, though at much lower temperature, does cause ignition by reason of its greater mass.

Dr. WYNNE said that in purifying carbon bisulphide for the purpose of determining its magnetic rotation, the late Mr. Rodger, by exposing the liquid to sunlight, had obtained some quantity of the brown substance with a view of determining its composition. The prevalent idea seemed to be that the brown substance was a sub-sulphide, possibly C_2S_3, and it would be interesting to know whether Professor Dixon had any evidence bearing on the point.

Professor SMITHELLS said that he could confirm Professor Dixon's remark as to the phosphorescent combustion of carbon disulphide. This substance might be added to the long list of carbon compounds which were capable of phosphorescent combustion. The combustion of carbon disulphide was of special interest from the fact that the flame did not exhibit the so-called carbon or candle spectrum, but this he believed could be explained by the masking effect of the burning sulphur. He had found that a burning mixture of ethylene and hydrogen sulphide gave no carbon spectrum, although an ethylene air flame of itself would of course do so. He had made some examination of the partial products of combustion of carbon disulphide; they were difficult to deal with, and he was glad that Professor Dixon had brought the inquiry to a successful issue. It was interesting to remark that some years ago Julius, from an examination of the spectrum of burning carbon disulphide, had concluded that some third substance besides carbon dioxide and water was formed, and he had detected carbon oxysulphide. Professor Dixon, however, had gone much further in establishing this fact.

*61. "*The Action of Nitric Oxide on Nitrogen Peroxide.*" By HAROLD B. DIXON and J. D. PETERKIN.

Some few years ago, the question was keenly debated whether nitrogen trioxide existed in the gaseous state. On both sides, the final appeal was made to the behaviour of nitric oxide when mixed with gaseous nitrogen peroxide. Ramsay and Cundall (*Trans.*, 1895, lxvii., 672) broke an inner tube, containing nitric oxide over mercury, by pressing it against an outer tube containing the peroxide over mercury. No contraction was observed. The experiment proved that no considerable quantity of trioxide could have been formed on mixing the gases. Lunge and Porschnew (*Zeit. Anorg. Chem.*, 1894, vii., 209) broke a thin glass diaphragm between a vessel containing nitric oxide and a similar one containing the peroxide. The gases showed a very slight expansion on diffusing "instead of

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the large contraction expected." The natural conclusion of chemists has been that "gaseous N_2O_3 apparently does not exist."

But the dissociation which nitrogen peroxide undergoes on diminution of pressure would have caused an appreciable expansion in these experiments if the nitric oxide had merely played the part of an inert gas.

The authors confirm Lunge and Porschnew's conclusion that a very slight alteration of volume occurs on mixing nitric oxide with the peroxide at 27°, but they show that a considerable expansion occurs when the peroxide mixes with nitrogen and other inert gases, and that this observed expansion is in close agreement with that calculated from Willard Gibbs's formulæ for the dissociation of the peroxide. The authors infer from their experiments that at 27° nitric oxide and peroxide combine to a limited extent to form an unstable compound, which is largely dissociated at this temperature, and undergoes increasing dissociation as the temperature is raised. The reversibility of the equation $N_2O_3 = NO + NO_2$ affords an easy explanation of the behaviour of the mixed gases towards reagents.

Discussion.

Professor Ramsay congratulated Professor Dixon on having shown that in the gases evolved from nitrous anhydride, which consist chiefly of a mixture of nitric oxide and peroxide, a small amount of gaseous nitrous anhydride is to be detected. The power of this mixture of gases to react as N_2O_3 is thus explained. In 1885, he (Professor Ramsay) stated that, as the result of experiments showing that, in the main, the gases obtained from liquid anhydride consist of NO_2, N_2O_4, and NO, "it cannot be taken as conclusive that no nitrous anhydride is present in the gaseous state"; and Professor Dixon has found that a small proportion does so exist. The proof is valuable, inasmuch as it explains why the mixture of gases can act on sulphuric acid, be absorbed by soda, and act as a diazotising agent.

Professor Dewar said that, in his paper, "Studies on the Electric Arc" (*Proc. Roy. Soc.*, 1880, xxx., 85) experiments are described showing the amount and character of the oxides of nitrogen produced when an arc is maintained in a cool dry moving atmosphere. The quantity of oxides formed did not exceed 1 grm. per hour. As the solution of the oxides in concentrated sulphuric acid gave the same percentage of nitrogen whether treated directly with mercury or after careful dilution with water and subsequent titration of the solution with permanganate, it was inferred that the main product was gaseous nitrous anhydride.

Experiments are also described in an address on "Phosphorescence and Ozone" (*Proc. Roy. Inst.*, 1888, xii., 557), which have an important bearing on this question. A current of attenuated air was maintained in a small vacuum tube of the ordinary form, and after the passage of the electric discharge was allowed to expand into a glass cylinder 3 feet long and 6 inches in diameter, maintained at a pressure not exceeding 6 or 8 m.m. by means of a large air-pump. The result was the production of extraordinary phosphorescent effects in the stream of air. This phosphorescence is associated with the production of ozone and oxides of nitrogen, as it does not take place in the absence of oxygen. Recently, the phosphorescent glow was allowed to pass through some liquid air in order to condense and solidify the oxides of nitrogen and dissolve the ozone out of the moving, luminous gas stream. The result was that the clear liquid air soon became turbid from the formation of a precipitated greenish-blue solid. On filtering this off, it gave all the reactions of nitrous acid, and no ozone was found in solution. The colour of the body at the low temperature shows it was not N_2O_4, which is colourless. It might be, however, a mixture of nitric oxide and nitrous anhydride. On the other hand, it is possible that NO_2, the dissociated molecule of N_2O_4, may exist in the solid state at a very low temperature and be coloured.

Mr. C. E. Groves said that, many years ago, in the course of experiments on the preparation of nitrosyl sulphate, he had found that the brown vapours given off when arsenious anhydride was heated at 70° with nitric acid of sp. gr. = 1·3 were almost entirely absorbed by concentrated sulphuric acid. Crystalline nitrosyl sulphate was formed, and but little, if any, nitric acid, although the latter should have been produced if nitric peroxide had been present. More recently, he had observed that these same vapours, when passed into a mixture of crushed ice and water, were absorbed, forming a solution of nitrous acid.

Professor Tilden said it was generally acknowledged that nitrogen trioxide existed only in the form of the blue liquid, which becomes almost completely dissociated by vaporisation. Professor Dixon seemed to have proved that in this case, as in so many others, a dissociable compound is more stable in the presence of the products of its dissociation.

*62. "*On the Mode of Burning of Carbon.*" By Harold B. Dixon.

In the combustion of carbon, the formation of carbon dioxide is usually described as being due to a single and direct action between carbon and oxygen; it is stated or implied that carbon monoxide is only formed by a secondary action between carbon dioxide and carbon. The only experiments which claim to prove this are the two series made by Julius Lang (*Zeit. Phys. Chem.*, 1888, ii., 168).

The author repeated Lang's experiments, and found that when oxygen was passed over carbon heated to 500° (a temperature at which Lang showed carbon dioxide was not reduced by carbon), even in a very slow stream, some carbon monoxide was always formed.

Under conditions far less favourable for the reduction of carbon dioxide than in Lang's experiments, viz., by passing a mixture of carbon dioxide with 6—8 per cent of oxygen over carbon heated to 500°, some carbon monoxide was always formed.

Lang's more important argument depends on his second series of experiments, which consisted in passing a mixture of oxygen, carbon monoxide, and nitrogen over carbon at 500°. He found that with a slow stream, the carbon monoxide remained unchanged in amount, whilst all the oxygen was converted into carbon dioxide; with a quicker stream, the proportion of carbon monoxide increased considerably, but with a still quicker stream it was much reduced. The author has made many experiments to test these results. When a mixture containing about 80 per cent of oxygen and 20 per cent of carbon monoxide, was passed quickly over coke heated to 500°, the blue flame of burning carbon monoxide was observed, and the amount of that gas found in the products was small. On lowering the rate of the gas stream, the flame was not formed, but the carbon glowed and the amount of carbon monoxide in the products increased. This reached a maximum and then diminished as the rate of the stream was continually lowered. With a very slow stream, from 2—4 per cent of carbon monoxide was found in the products. These results are quite opposed to the conclusions drawn by Lang, viz., that carbon monoxide is unaltered when mixed with oxygen, it is passed very slowly over carbon at 500°. His argument that carbon dioxide must be first formed is therefore invalid.

The results of the new experiments might be explained on either hypothesis if it be assumed that the molecule of the monoxide, or of the dioxide, as the case may be, formed by the direct union of the elements at 500°, retains sufficient heat (from its heat of formation) to react with oxygen or carbon respectively. The experiments of Baker (*Phil. Trans.*, 1888, clxxix. A, 571), make it very probable that the carbon burns first to carbon monoxide.

Discussion.

Professor Clowes said that Haldane (*Trans. Inst. Mining Engineers*, xvi., 470), had shown that a small pro-

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portion of carbon monoxide accompanied carbon dioxide in the products of the spontaneous oxidation of coal at ordinary temperatures. The carbon monoxide was detected by the reaction with diluted blood, its proportion was estimated by this colorimetric method, and the result confirmed by the ordinary gasometric method.

*63. "*Crystalline Glycollic Aldehyde.*" By Henry J. Horstman Fenton and Henry Jackson.

It has previously been shown by one of the authors (*Trans.*, 1895, lxvii., 774), that dihydroxymaleic acid, when heated with water, breaks up almost quantitatively into glycollic aldehyde and carbon dioxide, $C_4H_4O_6 = C_2H_4O_2 + 2CO_2$.

The resulting solution, after purification by treatment with calcium carbonate and extraction with alcohol, yields on evaporation in a vacuum, a colourless, sweet syrup, which was shown to be the aldehyde in nearly a pure state. Traces of the solvent used for purification, however, are obstinately retained, and various attempts have been made to obtain the substance absolutely pure.

It was further shown (*Trans.*, 1897, lxxi., 375) that this syrup, when heated to 100° in a vacuum, polymerises to a large extent, giving a hexose, $C_6H_{12}O_6$. During this operation, a small quantity of crystalline substance was often observed in the exit tube of the apparatus employed, but the quantity was too minute for thorough examination. By taking certain precautions, the authors now find that this crystalline substance can be obtained in fair quantity, that it is invariably produced in the process referred to, and on examination proves to be pure glycollic aldehyde.

Molecular weight determinations by the cryoscopic method indicate that, in the crystalline state, the substance is probably bimolecular, the numbers obtained when the solution is first made approximating to those required for the double formula, $C_4H_8O_4$. But on allowing the solution to stand, this value diminishes, and, after about 24 hours, becomes constant, and agrees almost exactly with that required for the single formula. This behaviour is quite analogous to that which Wöhl observed in the case of crystalline glyceraldehyde (*Ber.*, 1898, xxxi., 2394).

*64. "*On the Blue Salt of Fehling's Solution and other Cuprotartrates.*" By Orme Masson and B. D. Steele.

In this paper, electrolytic and chemical experiments are described which prove (*a*), that the blue salt contains a complex negative radicle of which copper is a part; (*b*), that none of the copper plays an electropositive part; (*c*), that when a current passes through the blue solution, copper is deposited on the cathode by secondary action of the *K* ions there; (*d*), that the blue solution may be prepared perfectly neutral to litmus by the interaction of cupric tartrate and alkali in the ratio of 5KOH to $4CuC_4H_4O_6$, and that this neutral solution contains $K_2C_4H_4O_6$ as well as the blue salt; (*e*), that the latter may be completely purified by precipitating it with alcohol; (*f*), that when dried in vacuo it has the composition $K_8C_{12}H_9Cu_4O_{19}.4H_2O$; (*g*), that it gives rise to the production, by double decomposition, of a series of salts of the heavy metals, obtained as more or less insoluble, blue, amorphous precipitates, of which the silver and lead salts have been analysed; (*h*), that the free acid corresponding to these cuprotartrates is unstable and, so far, unobtainable; (*i*), that excess of alkali converts the neutral blue cuprotartrate into a strongly alkaline salt, which is also capable of being separated by alcohol.

Discussion.

Dr. Thorne said the blue salt has been recently examined in his laboratory by his assistant, Mr. E. H. Jeffers. It had been obtained by precipitation as a viscid liquid gradually depositing crystals, but it had not yet been isolated in a pure state. It was readily soluble in water, and the aqueous solution did not show any decomposition on boiling.

It is remarkable that the whole of the copper should be present in the negative condition. The complicated formula assigned to the salt seemed improbable, as Luff has recently (*Zeits. Ges. Brauw.*, 1898, xxi., 319) described a potassium cupric citrate, $K_2Cu(C_6H_4O_7),6H_2O$, obtained in an analogous way. This latter salt appears to be an ordinary double salt with the copper in the positive condition, but its behaviour with reducing sugars is similar to that of the tartrate described.

*65. "*The Preparation of Acid Phenolic Salts of Dibasic Acids.*" By S. B. Schryver, D.Sc., Ph.D.

When the sodium salt of a phenol is treated with the anhydride of an organic dibasic acid in the presence of a liquid, such as a hydrocarbon, which exerts no chemical action on either the phenol sodium salt or the anhydride, a reaction takes place, which may be represented by the following general equation:—

$$R{<}\begin{matrix}CO\\CO\end{matrix}{>}O + XONa = R{<}\begin{matrix}COOX\\COONa\end{matrix},$$

where R = residue of an organic dibasic acid, X = a phenylic group.

The hydrocarbon most generally employed was xylene. The phenol was dissolved in about ten times its weight of the hydrocarbon, and the sodium salt prepared by the direct action of metallic sodium on this solution. On adding the anhydride, an immediate action takes place in most cases, and the sodium phenolic salt separates out on standing in the form of a gelatinous mass. This can be dissolved up in water and thus separated from the hydrocarbon, and the acid phenolic salt can be precipitated from the aqueous solution of the sodium salt thus obtained by the addition of dilute mineral acids. By means of the reaction, the following substances were prepared:—

Phenol hydrogen camphorate—
$CO_2H{\cdot}C_8H_{14}{\cdot}CO_2(C_6H_5)$, m. p. 100°.

Thymol hydrogen succinate—
$CO_2H{\cdot}C_2H_4{\cdot}CO_2(C_{10}H_{14})$, m. p. 121—122°.

Thymol hydrogen phthalate—
$CO_2H{\cdot}C_6H_4{\cdot}CO_2(C_{10}H_{14})$, m. p. 132·5°.

Thymol hydrogen camphorate—
$CO_2H{\cdot}C_8H_{14}{\cdot}CO_2(C_{10}H_{14})$, m. p. 89°.

Guaiacol hydrogen succinate—
$CO_2H{\cdot}C_2H_4{\cdot}CO_2(C_6H_4{\cdot}OCH_3)$, m. p. 75°.

Guaiacol hydrogen camphorate—
$CO_2H{\cdot}C_8H_{14}{\cdot}CO_2(C_6H_4{\cdot}OCH_3)$, m. p. 112°,

from which the neutral salt, $C_8H_{14}(CO_2C_6H_4{\cdot}OCH_3)_2$, m. p. 124°, was prepared, β-Naphthol hydrogen camphorate, $CO_2H{\cdot}C_8H_{14}{\cdot}CO_2C_{10}H_7$, m. p. 120—121°. Eugenol hydrogen camphorate, m. p. 115·5°. Carvacrol hydrogen camphorate, a syrup.

As will be seen from the above examples, the reaction is applicable to a large number of phenols and acid anhydrides, but it does not apply, however, universally. So far, two classes of exceptions have been discovered amongst substituted phenols.

(1). The ortho- and para-nitrophenols.—Whereas the sodium salt of metanitrophenol dissolves readily in a 10 per cent solution of camphoric anhydride in xylene, neither the corresponding ortho- nor para-compounds react, even when heated to 180° in a sealed tube. Reference is made to the differences in the reaction of meta-compounds, as opposed to the corresponding ortho- and para-compounds, in the publications of Menschutkin (*Ber.*, 1897, xxx, 2968) and Lobry de Bruyn (*Rec. Trav. Chem.*, 1894, xiii., 101—147). The metanitrophenol camphorate, $CO_2H{\cdot}C_8H_{14}{\cdot}CO_2C_6H_4{\cdot}(NO_2)$, prepared by the reaction, commences to melt at 115°, but is not completely molten till some degrees higher.

(2). Diortho-substituted phenols.—A series of bromo-compounds was prepared, viz., *p*-bromophenol, 2 : 4-dibromophenol, 2 : 6-dibromophenol, 2 : 4 : 6-tribromophenol. 2 : 6-Dibromophenol was obtained by the reduction of 2 : 6-dibromoparanitrosophenol (OH = 1) and subsequent replacement by hydrogen of the amino-group

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in the product thus obtained by means of ethyl nitrite. The other bromophenols were obtained by direct bromination.

It was found that, whereas *p*-bromophenol and 2 : 4-dibromophenol readily reacted with camphoric anhydride yielding camphorates, $CO_2H\cdot C_8H_{14}\cdot CO_2C_6H_4Br$, and $CO_2H\cdot C_8H_{14}\cdot CO_2C_6H_3Br_2$, melting respectively at 111° and 173°, neither the 2 : 6-dibromophenol nor the 2 : 4 : 6-tribromophenol reacted, even when heated to 180° in a sealed tube. This non-reactivity is analogous to the non-formation of alkyl salts of diortho-substituted benzoic acids (compare V. Meyer and Sudborough, *Ber.*, 1894, xxvii., 510, 512, 1580, 3146). V. Meyer ascribes the non reactivity to stereochemical causes. In this case, as well as in the reactions described above, it seems doubtful whether the non-reactivity is to be ascribed to the presence merely of two substituted groups in the ortho-position (stereochemical causes), or to the close proximity of two strongly negative groups—in other words, to statical or dynamical causes—especially when the fact is taken into account that even certain mono-substituted products are incapable of reacting.

DISCUSSION.

Dr. LAPWORTH thought that Dr. Schryver's observations afforded further evidence in favour of the view that in the salts of ortho- and para-nitrophenols the constitution of the nucleus is no longer benzenoid, but quinonoid; that is to say, that the salts are derivatives of isonitro-compounds analogous to quinoneoximes, and not to true phenols. In the case of metanitrophenol, as the migration of the phenolic hydrogen into the nitro-group is not possible, and as nitrobenzenes do not form salts, it is probable that the salts of metanitrophenol are true phenolates.

66. "*The Maximum Pressure of Naphthalene Vapour*," By R. W. ALLEN, M.A.

An accurate knowledge of the amount of naphthalene required to saturate a given volume of gas at various temperatures is of great importance to gas engineers. The author has therefore determined the vapour pressure of naphthalene both by the "evaporation" and the "barometric" methods, and obtained results which are in entire accord, but which differ notably, especially at the lower temperatures, from the few measurements given by Naumann. The paper contains tables giving the pressures obtained by both methods as well as one giving the weight of naphthalene required to saturate a cubic metre of gas at temperatures varying from 0° to 130°.

67. "*Scoparin*." By ARTHUR GEORGE PERKIN.

Scoparin, the colouring matter of broom (*Spartium Scoparium*, *L.*) was discovered by Stenhouse (*Annalen*, 1851, lxxviii., 17), who assigned to it the provisional formula $C_{21}H_{22}O_{10}$ (mean of analyses, C = 57·67; H = 5·34). Hlasiwetz (*Annalen*, 1866, cxxxviii., 190) included scoparin in the quercetin group, for, on fusion with alkali, it gave phloroglucinol and protocatechuic acid.

The similarity of the dyeing properties of scoparin and vitexin pointed to their close relationship (*Trans.*, 1898, lxxiii., 1019. The results of Stenhouse and Hlasiwetz (*loc. cit.*) have been confirmed, as analysis gave C = 57·60, H = 5·09, and fusion with alkali at 220°, phloroglucinol and protocatechuic acid. Digested with hydriodic acid, one molecule of methylic iodide is evolved (found, CH_3 = 3·88), and a new colouring matter, *scoparesin*, results, distinguished from scoparin by its strong tinctorial properties. With boiling potassium hydrate solution, scoparin gives phloroglucinol, vanillic acid, and a third substance, $C_9H_{10}O_3$ (found, C = 64·82; H = 6·17) colourless needles m. p. 114°. As this latter contains one methoxy-group (found, CH_3 = 9·65), reacts with semicarbazid, and on fusion with alkali gives protocatechuic acid, it is a *dihydroxyacetophenonesmonomethyl ether* (probably OH ; OCH_3 : $COCH_3$ = 1 : 2 : 4).

Solutions of vitexin and scoparin in sulphuric acid, when heated, both develop a dull green colouration. The former, by decomposition with alkali, gives *p*-hydroxy-acetophenone and phloroglucinol, and it is thus very probable that scoparin is a *methoxy-vitexin*. The author intends to investigate this colouring matter further.

68. "*On a new Compound of Arsenic and Tellurium*." By E. C. SZARVASY, Ph.D., and C. MESSINGER, Ph.D.

Whilst investigating the compounds which arsenic forms with the elements of the oxygen group, a regularity in their properties was observed, which led to the discovery of a new telluride. The investigation aimed chiefly at a study of the behaviour of these compounds at high temperatures, and the determination of their molecular weights by means of their vapour densities.

Selecting from each group of the compounds examined those most stable at high temperatures, a certain numerical regularity was observed between their molecular weights. In the series of compounds having the formulæ As_2O_3, As_2S_3, As_2Se, the differences between the molecular weights of such a series are 16 and 15 units respectively. Similarly, we may determine the formula of the next probable tellurium compound higher in the series, having the same difference between it and the preceding member. Calculation indicated the formula of this compound to be As_8Te_3. It was subsequently prepared by melting its components together in the ratio 8As : 3Te in a sealed tube under pressure. The vapour density of this compound was also determined. The paper concludes with a comparison of the properties of the compounds which arsenic forms with the various elements of the oxygen group.

69. "*The Action of Hydrogen Peroxide on Secondary and Tertiary Aliphatic Amines. Formation of Alkylated Hydroxylamines and Oxamines.*" By WYNDHAM R. DUNSTAN and ERNEST GOULDING.

In a previous communication (*Proc.*, 1899, xv., 58), the authors have shown that methyl iodide reacts with hydroxylamine, forming *trimethylamine oxide* or *trimethyloxamine*, $(CH_3)_3N{:}O$, whilst ethyl iodide forms first *β-diethylhydroxylamine*, $(C_2H_5)_2NOH$, and by further action *triethyloxamine*, $(C_2H_5)_3N{:}O$.

The constitution of these oxamines suggested the possibility of their formation from the corresponding amines by the action of weak oxidising agents. The authors find that trimethylamine is readily oxidised in aqueous solution by standing in the cold with a dilute solution of hydrogen peroxide, forming *trimethyloxamine* identical in properties with the compound already described. Similarly, triethylamine is readily oxidised to *triethyloxamine*. In both cases, the yield is nearly quantitative. Diethylamine, under the same conditions, is converted into *β-diethylhydroxylamine* identical with the compound prepared by the authors by the reaction of ethyl iodide with hydroxylamine. Experiments are now being made with other amines and with ammonia.

70. "*The Enantiomorphously Related Tetrahydroquinaldines.* By WILLIAM JACKSON POPE and STANLEY JOHN PEACHEY.

Dextrotetrahydroquinaldine was obtained by Ladenburg (*Ber.*, 1894, xxvii., 77) by crystallising the externally compensated base with tartaric acid, when dextrotetrahydroquinaldine bitartrate is eventually obtained in a state of purity. Lævotetrahydroquinaldine has not previously been prepared.

On dissolving externally compensated tetrahydroquinaldine in hot water, by addition of a half-molecular proportion each of hydrochloric and dextro-*a*-bromocamphorsulphonic acids, and allowing to cool, *lævotetrahydroquinaldine dextro-a-bromocamphorsulphonate*,—

$$C_{10}H_{13}N,C_{10}H_{14}BrO\cdot SO_3H,$$

separates in almost quantitative yield. The salt is sparingly soluble in water, and is purified by two or three re-crytallisations from alcohol; it crystallises in colourless needles melting at 218—220°, and on treatment with soda the base separates as an oil, which is extracted

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with ether and purified by distillation under reduced pressure.

Lævotetrahoydroquinaldine, $\begin{matrix}CH:CH\cdot C\cdot CH_2\cdot CH_2\\ |\quad\quad |\quad\quad |\\ CH:CH\text{-}C.NH.CHMe\end{matrix}$, is a colourless, highly refractive oil, of faint basic odour, and boils at 158° under 59 m.m. pressure. It has a specific gravity of 1·0236 at 14·5°/4°, and gives the rotation $\alpha_D = -58·60°$ in a 100° m.m. tube at 16°; the specific rotation is therefore $[\alpha]_D = -57·25°$. For the relations of the dextro-isomeride, Ladenburg gives $\alpha_D = +58·35°$ and $[\alpha]_D = +55·99°$ having apparently used the density of the externally compensated base in calculating the specific rotation.

Benzoyl-lævotetrahydroquinaldine, $C_{10}H_{12}N\cdot COPh$, is readily obtained, by shaking the base with dilute soda and benzoyl chloride, as a granular crystalline mass, which is purified by crystallisation from ethyl acetate. It separates from cold acetone in lustrous colourless monosymmetric prisms melting at 117—118°, and has the specific rotation $[\alpha]_D = +247·3°$ in a 3·5 per cent benzene solution. A comparison of its properties with those of Walter's optically inactive benzoyltetrahydroquinaldine (*Ber.*, 1892, xxv., 1261) shows that the latter is a true racemic compound.

After filtering off the lævotetrahydroquinaldine dextro-α-bromocamphorsulphonate, the mother-liquor is made alkaline, and the crude dextrotetrahydroquinaldine extracted with ether, and converted into dextrocamphorsulphonate by addition of the requisite quantity of Reychler's camphorsulphonic acid (*Bull. Soc. Chim.*, 1898, [iii.], xix., 120); a crystalline substance separates, which, after repeated re-crystallisation from acetone, yields *dextrotetrahydroquinaldine dextrocamphorsulphonate*,—

$$C_{10}H_{13}N,C_{10}H_{15}O\cdot SO_3H.$$

This salt crystallises in colourless needles melting at 127—128°, and has the specific rotation $[\alpha]_D = +45°$ in a 4 per cent aqueous solution; it yields Ladenburg's dextrotetrahydroquinaldine when treated with soda. *Lævotetrahydroquinaldine dextrocamphorsulphonate*,—

$$C_{10}H_{13}N,C_{10}H_{15}O\cdot SO_3H,$$

also crystallises well, separating from acetone solution in long colourless needles melting at 137—138°; it has the specific rotation of $[\alpha]_D = -16°$.

Benzoyldextrotetrahydroquinaldine, $C_{10}H_{12}N\cdot COPh$, is completely analogous to its enantiomorphously related isomeride; it melts at 117—118°, and has the specific rotation of $[\alpha]_D = -247·4°$ in a 4 per cent benzene solution. The benzoyl derivatives now described are hydrolysed by prolonged boiling with hydrochloric acid, yielding benzoic acid and the original base.

PHYSICAL SOCIETY.

Ordinary Meeting, May 12th, 1899.

Professor PERRY, Vice-President, in the Chair.

DR. LEHFELDT read a note on "*The Vapour-pressure of Solutions of Volatile Substances.*"

The change in vapour-pressure of a solvent due to the solution in it of a small quantity of volatile material has been calculated on the basis of Raoult's note for the corresponding case of a non-volatile dissolved body. The author has interpreted the formula of Nernst in the following words:—When a small quantity of volatile substance is dissolved in a liquid, the vapour-pressure of the liquid is altered in the ratio of the molecular fractional amount of solvent in the liquid to that in the vapour. In order to test this formula it has been applied to the results of experiments made on four series of liquids, viz., alcohol with benzene and toluene, and carbon tetrachloride with benzene and toluene. In the case of normal solutions—such as carbon tetrachloride in toluene, carbon tetrachloride in benzene, and benzene in carbon tetrachloride—the agreement between the observed and calculated values of the percentage composition of the liquid was remarkably good. In the case of toluene in carbon tetrachloride the solution contained about 29 per cent of the dissolved body, and, as the range of applicability of the formula had probably been exceeded, the agreement was not so good as in the previous examples. The mixtures containing alcohol show maxima of vapour-pressure, and on this account the departure from the formula is so much more marked that it is impossible to apply it except in the case of very dilute solutions. The temperature used throughout the experiments was 50° C.

The SECRETARY read a note by Prof. W. B. Morton and Dr. Barton on the discussion of their paper "On the Criterion for an Oscillatory Discharge of a Condenser." In the discussion which followed the reading of the paper it was pointed out that the result obtained, viz., that on taking into account the distribution of the current in the wire, a condenser having the critical capacity on the simple theory gives an oscillatory discharge, seems to be contradicted by the well-known fact that the resistance of the wire is greater and the inductance less for oscillatory than for steady currents. The explanation of the apparent paradox is to be found in the effect of the damping on the inductance. When the damping is great and the frequency small, as in the neighbourhood of the critical case, what may be termed the equivalent inductance becomes greater than the steady current value. It is shown that this increase in "L" outweighs the increase of "R" in its effect upon the criterion for oscillatory discharge. An examination of the expression for the equivalent inductance in the case of iron shows that it is greater than the steady-current value if the ratio of one amplitude to the next is greater than $\epsilon^{\frac{n}{100}}$ where n is the frequency of the oscillation. Since the decrease of "L" with maintained oscillations is due to a surface concentration of current, it is suggested that there must be an axial concentration in the case of damped vibrations. Following the method of Maxwell for determining the current density at a distance from the axis of a wire, an expression for the current was introduced containing a damping coefficient. The "quasi-amplitude" of the disturbance at any point in the wire was thus obtained. An examination of the result shows that making the damping zero indicates a surface concentration. If, on the other hand, the damping is great, the expression for the amplitude increases as the distance from the axis decreases, and we get an axial concentration. Assuming sufficient damping to produce this effect, is is shown that as we go through the point—

$$r = \frac{a}{\sqrt{2}},$$

where "a" is the radius of the wire we pass from a greater value of current density in the inner parts to a less in the outer than would correspond to a uniform distribution throughout the wire. From general reasoning the authors think that if a rapidly damped disturbance is propagated into a wire from its boundary, and if the oscillations are slow enough to allow the current to penetrate to the core, we should expect to find an axial concentration in the latter stages of the phenomenon.

Dr. LEHFELDT said that Prof. Lodge had pointed out, at the reading of the paper, that the solution the authors obtained changed character at the critical resistance. As this point had not been considered in the note, he supposed that the change in character made no difference to the results obtained.

The CHAIRMAN expressed his interest in the proof of the existence of an axial concentration.

Mr. ADDENBROOKE exhibited and described a quadrant electrometer for application to alternating current measurements. The author has substituted for cylindrical quadrants two sets of flat plates, the top set being adjust-

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able. In this way the range of the instrument is considerably increased. The ability to remove one or more of the top quadrants makes the needle very accessible. By lowering the needle on to the bottom quadrants, and then bringing down one of the top plates, the instrument can be carried with safety. One of the top quadrants can be worked up and down with a worm gear, and by this motion the "electrical zero" of the electrometer is obtained. The suspension consists of a flat phosphor bronze strip, the torsion of which is found to be perfectly uniform, there being no fatigue effect. The case of the instrument contains windows, so that the needle can be viewed from two directions at right angles, and there are screw motions to centre the needle with respect to the quadrants. To reduce the effect of air convection currents upon the needle, the inside of the case is lined with cotton velvet. The quadrants are supported on brass bars passing through long ebonite sleeves in the bottom of the instrument. This gives good insulation without the use of sulphuric acid, and there is no Leyden jar or condenser in connection with the needle. Whan using the electrometer idiostatically, with the finest strip, a light needle, and the quadrants one-tenth of an inch apart, a difference of potential of 1 volt will produce a deflection of about 5 m.m. upon a screen 2 metres distant. Using the instrument heterostatically, with 100 volts on the needle, one-fifth of an inch between the quadrants and half a volt acting across them, a deflection of 200 m.m. can be obtained. This sensitiveness is about twelve times as great as that got from instruments designed by Kelvin, Mascart, and Haga. Mr. Addenbrooke then showed how, in conjunction with a voltmeter and an ammeter, it was possible with his instrument to determine all the factors of an alternating current system. One increased sensitiveness of the electrometer renders it possible to measure currents of any magnitude with a very small waste of energy.

Mr. GASTER pointed out that the measurement of self-induction with an electrometer could only be carried out practically if the current curve was a sine curve. He said that in curves obtained from a Ganz motor a correction amounting to 7 per cent had to be applied.

The CHAIRMAN said that even if the curve obtained was a sine curve, the electrometer was never used in this country for measuring self-induction.

Prof. HERSCHELL asked if it were possible to adjust the quadrants after the needle had been charged.

Mr. ADDENBROOKE then purposely disturbed the position of the adjustable plate, and, after charging the needle, reduced the deflection to zero by the worm gear. The author said that for high voltages the curve of calibration was different to that obtained from the ordinary formula.

The CHAIRMAN said that this discrepancy was probably due to want of perfect symmetry. In a paper read before the Royal Society, by Perry, Ayrton, and Mather, it was shown that the presence of the guard around the mirror of an ordinary electrometer was sufficient to affect the needle when working with high voltages. In working with the plates very close together, he was afraid the symmetry would be liable to be disturbed by a slight tilting of the needle due to electrostatic attraction.

The author observed that the plates were only very close together when working with low voltages.

The VICE-PRESIDENT proposed votes of thanks, and the meeting adjourned until May 26th.

CORRESPONDENCE.

THE 32 EQUIVALENT AND ITS RELATION TO THE PERCENTAGE OF AVAILABLE SODA IN CAUSTIC SODA.

To the Editor of the Chemical News.

SIR,—The letters by Mr. Pattinson and Prof. Lunge referring to my letter in the CHEMICAL NEWS of March 30th (vol. lxxix., p. 155) have been read by me with great interest.

I regret Prof. Lunge considers it necessary to include my method of calculation amongst the erroneous methods—which he assumes I have not observed—quoted on page 106, vol. ii., of his book. The reason I expressed my astonishment at Prof. Lunge in my letter was based principally on the perusal of the above-mentioned page of his magnificent work.

I must apologise to Prof. Lunge, and also Mr. Pattinson, for having attributed the compilation of the table under dispute to the wrong person.

I regret I cannot agree with Mr. Pattinson's argument referring to his table and the "Tyne" test.

To my mind it resolves itself into a matter of how the standard acid is prepared, and the old-established law of equivalents.

With regard to the preparation of the standard acid, we find the following statement in Lunge (vol. ii., p. 106):—

"On the Tyne the equivalent of sodium carbonate was taken at 54 instead of 53, and the test-acid made so that a litre of it saturates 54 grms. pure Na_2CO_3."

Mr. Pattinson states in his letter that the test-acid on the 32 equivalent is weaker than the true normal acid!

Let us assume that Prof. Lunge's description of preparing the test-acid is the basis of the method generally adopted—which it must be, unless somebody is making an awful mistake—and apply the principle of equivalents to it. Thus, a normal acid which saturates 54 parts Na_2CO_3 will neutralise 41 parts NaHO or 32 parts Na_2O, which means that a sample of pure caustic soda tested with this acid would yield 78·05 per cent Na_2O. Take a simple example to illustrate:—Weigh out 4·1 grms. NaHO, and assume it required 100 c.c. test-acid to neutralise it; then the sample would contain—

$\frac{100 \times 4{\cdot}1}{4{\cdot}1} = 100$ per cent NaHO or $\frac{100 \times 3{\cdot}2}{4{\cdot}1} = 78{\cdot}05$ per cent Na_2O. Am I not, therefore, justified in saying that Mr. Pattinson's table is wrong, as far as caustic soda is concerned?

With regard to the abolition of the 32 equivalent, is it not a matter for the consumers to take up? The manufacturers can hardly be expected to take action on their own account.—I am, &c.,

H. A. HOOPER.

Chicago, Ill., U.S.A., May 1, 1899.

CHEMICAL NOTICES FROM FOREIGN SOURCES

NOTE.—All degrees of temperature are Centigrade unless otherwise expressed.

Comptes Rendus Hebdomadaires des Séances, de l'Académie des Sciences. Vol. cxxviii., No. 17, April 24, 1899.

Furfuric Alcohol.—G. André.—Furfuric alcohol, $C_5H_6O_2$, is a substance about which little is known. It is difficult to prepare in large quantities and spontaneously alters after a few hours. The author has repeated Hugo Schiff's preparation with many refinements, to obtain the substance in a state pure enough for determining its heat of formation, to complete the series of thermal relations recently found by MM. Berthelot and Rivals. Furfurol is placed in contact with very slight excess of concentrated aqueous potash solution. The mixture becomes heated and turns into a reddish mass. The furfuric alcohol dissolves in water together with pyromucate of potassium and the unattacked furfurol. This aqueous solution is saturated with CO_2, and then the alcohol extracted with ether. The author obtained by this method,

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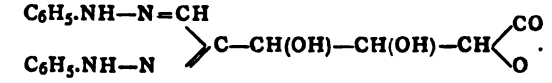
after many rectifications, a colourless liquid boiling at 87—89°, and givingon analysis the formula $C_5H_6O_2$.

Oxycellulosic Osazones.—Leo Vignon.—The author has previously shown that cotton absorbs phenylhydrazine. He now publishes his researches on the precise reaction which takes place when phenylhydrazine acts on the cellulose of cotton and some of the derivatives of oxidation. The formation of osazones from oxycelluloses corroborates the hypothesis that has already been stated about the oxycellulosic molecule. The osazone group of the oxycelluloses would be—



Journal de Pharmacie et de Chimie, Series 6, Vol. ix., No. 1.

The Transformation of the Carbonate of Orthocresol into a Homologue of Orthocresol Phthalein.—P. Cazeneuve.—Already inserted.

No. 2.

The Action of B. Coli and of Eberth's Bacillus on the Nitrates.—L. Grimbert.—This has already been inserted in full.

MEETINGS FOR THE WEEK.

MONDAY, 22nd.—Royal Institution, 5. Adjourned General Meeting.

TUESDAY, 23rd.—Royal Institution, 3. "Recent Advances in Geology," by Prof. W. J. Sollas, D.Sc., F.R.S.

THURSDAY, 25th.—Royal Institution, 3. "Water Weeds," by L. C. Miall, F.R.S.

FRIDAY, 26th.—Physical, 5. "On the Thermal Properties of Normal Pentane" (Part 2), by Prof. S. Young and Mr. Rose-Innes. "On the Distribution of Magnetic Induction in a Long Iron Bar," by C. G. Lamb.

—— Royal Institution, 9. "Climbs and Explorations in the Andes," by Sir William Martin Conway, M.A.

SATURDAY, 27th.—Royal Institution, 3. "The Music of India and the East, and its Influence on the Music of Europe" (with Musical Illustrations), by Edgar F. Jacques.

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THE CHEMICAL NEWS.

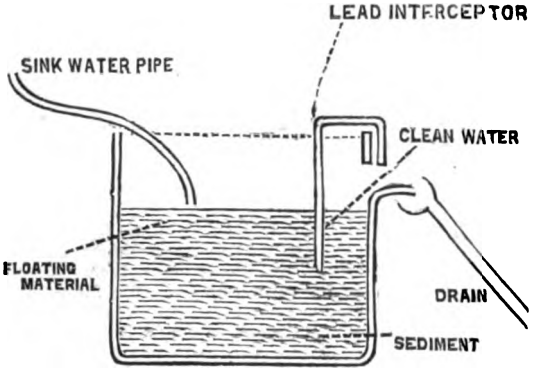
Vol. LXXIX., No. 2069.

SEDIMENT TRAP.

By ARTHUR H. COOTE.

The accompanying sketch explains a very useful addition to the sediment traps in common use in chemical laboratories.

It consists of a piece of sheet-lead bent twice at right-angles, so as to fit across the trap, and be supported in its



place by the front and sides of the trap. It effectually prevents paper, matches, corks, &c., either from choking the outlet and causing the trap to overflow or from passing into the drain itself.

A plumber can fit any number of such in a very little time.

Ordnance College, Woolwich,
May 9, 1899.

A NEW METHOD FOR THE ESTIMATION OF CARBONIC OXIDE.

By MM. SCHLAGDENHAUFFEN and PAGEL.

M. Nicloux has recently published a method for the estimation of carbonic oxide, based on the oxidation of this gas on contact with anhydrous iodic acid at a temperature of 150°, according to the following reaction:—
$5CO+2IO_3H=5CO_2+H_2O+I_2$.

The apparatus of which he makes use is arranged so as to absorb the iodine by means of a weak solution of caustic soda. When the operation is ended we add a little nitrite of soda and sulphuric acid until the reaction is distinctly acid; agitate with sulphide of carbon, and titrate the more or less coloured solution by comparison with a typical solution containing a known quantity of iodine.

On examining the very simple equation of this reaction it seemed probable to us that other oxygenated compounds might behave in a similar manner. We therefore undertook a first series of experiments with molybdic, chromic, arsenic and arsenious, stannic, antimonic and antimonious acids, but without the slightest success, since none of them was reduced either at 150° or at higher temperatures varying between 200° and 300°.

Following up these negative results, we commenced a new series of operations with some metallic oxides,—oxides of silver, lead, bismuth, and copper,—with the following results:—

1. *Oxide of Silver.*—Oxide of silver, previously dried in an air-oven at a temperature of 150° and placed in a U-tube in a water-bath, is submitted to the action of a current of pure carbonic oxide, absolutely free from carbonic acid, by means of a flask filled with baric hydrate. On leaving the experimental tube the gaseous current passed through another barytic solution which begins to become cloudy when the temperature reaches 50°. Between 54° and 60° the white precipitate becomes very abundant, and thus indicates the presence of a large proportion of carbonic acid. At the same time the colour of the oxide of silver changes; the original dark brown colour gives place to a brilliant white appearance. By gently shaking the U tube, so as to allow the gas to penetrate the pulverulent material more intimately, we find that the operation is terminated after the lapse of a few minutes. The deoxidation of the metallic oxide is thus effected, and the carbonic oxide is transformed into carbonic acid.

To decide whether it is possible to formulate this experiment thus, $CO+Ag_2O=CO_2+Ag_2$, we substituted for the barytic solution a Liebig's tube filled with potash at 50 per cent, weighed before and after the passage of the gas. With 2 grms. of oxide of silver we observed, under the same conditions as to temperature as above, a loss of 0·145 grm. of oxygen. The corresponding quantity of carbonic acid is by calculation 0·385 grm: this figure is absolutely the same as that given by the increase of weight of the potash tube, which, therefore, proves that the experiment is entirely in accord with theory, and that the above formula is justified.

2. *Cuprous Oxide.*—We take cuprous oxide, heated in the air-oven to 150°, and proceed as above, placing the U-tube in a water-bath, but nothing comes over even when the water is boiled; the barytic solution does not become cloudy. By using an oil-bath we notice a slight cloudiness at about 125°. The precipitate of carbonate of baryta becomes abundant at 215°; at this moment the colour of the material in the tube changes, becoming red, instead of brown as it was originally. Then, towards 300°, we notice a lively incandescence take place, indicating the end of the operation, and the whole of the oxide is transformed into metallic copper, having a crystalline aspect. The reaction is effected in the same manner as the preceding one, viz., $CO+Cu_2O=CO_2+Cu_2$, from which we may safely say that it is the result of an estimation carried out under the same conditions as those with the oxide of silver. We have in fact:—

Oxygen used	2 grms.
Loss of oxygen	0·25 grm.
Theoretical amount of carbonic acid..	0·680 „
Carbonic acid found	0·685 „

The concordance between the two latter figures is perfect, since the temperature to which we carried the cuprous oxide was a little too high. At 150° the suboxide begins to change into cupric oxide; this is a source of error easy to prevent.

3. *Oxide of Bismuth.*—In submitting oxide of bismuth, dried at 150°, to the action of a current of carbonic oxide, on an oil-bath at 230°, the barytic solution through which the gas passes commences to become cloudy. The precipitate increases at 260°, at the same time as the colour of the material changes; it becomes yellow, instead of white as it was originally. Between 385° and 400° it becomes black, and changes into the suboxide, but not into metallic bismuth. This result might, however, be foreseen, as various writers agree that the suboxide is very difficult to reduce. If, instead of allowing the suboxide to cool in the experimental tube, we throw it out while still warm, it changes rapidly into Bi_2O_3 with bright incandescence.

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4. *Oxides of Lead.*—The oxidised compounds of lead behave in different manners on contact with carbonic oxide. With minium, for example, we notice that deoxidation already begins at 225°, while litharge does not appear to be attacked below 300°. The white oxide, derived from the hydrate, previously heated in the oven to 150°, is deoxidised with still greater difficulty. It gives metallic lead when the temperature of the oil-bath is carried to 430°, but the reaction is not so sharp as with the oxides of silver and copper, since the metal remains mixed with a certain quantity of suboxide, without, however, containing carbon, as stated by M. Boudouard in speaking of Lowthian Bell's experiments.

To sum up, the oxides of silver and copper, heated in a current of carbonic oxide, are entirely deoxidised, the first at 60°, the second at 300°, and may consequently serve to completely absorb this gas. As the carbonic acid formed corresponds theoretically with the oxygen lost, it follows that this reaction constitutes a new method for the estimation of carbonic oxide.—*Journ. de Pharm. et de Chim.*, Series 6, vol. ix,, No. 4.

ACTION OF THE METALLIC SULPHATES ON PARATUNGSTATE OF POTASSIUM.

By L. A. HALLOPEAU.

In a research on the acid tungstates, von Knorre described several double paratungstates, obtained by the reaction in the wet way, of some metallic sulphates on paratungstate of sodium.

I have found that the metallic sulphates react on paratungstate of potassium in an analogous manner; but the study of the products of the reaction is much more difficult than in the case of the sodium salt, on account of the paratungstate of potassium being less soluble. I was, however, enabled to distinctly obtain the following double paratungstates by this method:—

Paratungstate of Potassium and Magnesium.—This compound is prepared by mixing two solutions containing equal molecular weights of paratungstate of potassium and sulphate of magnesium. On concentration the double salt is deposited. It is almost completely insoluble in cold water, but can be dissolved in warm water, which enables us to purify it by a fresh crystallisation. The product thus obtained answers to the formula $12WO_3 5(2/3K_2O + 1/3MgO) + 24H_2O$.

	Found. I.	Found. II.	Calculated.
$12WO_3$	77·28	76·86	77·42
$10/3K_2O$	9·04	8·92	8·71
$5/3MgO$	2·09	2·41	1·86
$24H_2O$	11·60	11·89	12·01
	100·01	100·08	100·00

These crystals have, under the microscope, the appearance of prisms, sometimes taking the form of hexagonal tablets; they act strongly on polarised light, showing extinctions parallel to the direction of the axes. They lose 17 molecules of water at 100°, that is to say, 8·40 per cent—theory requires a loss of 8·50 per cent.

Paratungstate of Potassium and Manganese. — By mixing two solutions, containing equal molecular weights of paratungstate of potassium and sulphate of manganese, we instantly obtain a yellowish-white precipitate in the form of microscopic crystals, completely insoluble in water. After prolonged washing with warm water, this salt answers to the formula $12WO_3,3K_2O,2MnO + 16H_2O$. These crystals are colourless, rhomboidal prisms, with modified angles, very refrangible, and acting strongly on polarised light. They lose 10 molecules of water at 100°, that is to say, 5·21 per cent—theory requires 5·15 p. c.

	Found. I.	Found. II.	Found. III.	Calculated.
$12WO_3$	79·58	79·72	80·09	79·63
$3K_2O$	7·79	—	—	8·07
$2MnO$	4·74	4·40	—	4·06
$16H_2$	8·05	8·10	—	8 24
	100·16			100·00

There is also formed a compound, slightly soluble in water, when we pour a solution of sulphate of zinc into a solution of paratungstate of potassium; but the crystals of this salt are always accompanied by crystals of paratungstate of potassium, which separate out at the same time.

By the action of sulphate of calcium on paratungstate of potassium, we obtain an amorphous insoluble precipitate. The same thing occurs with most other metallic sulphates; but these insoluble double salts are often mixed with tungstic acid, especially when the solution of the sulphate is acid.—*Bull. Soc. Chim.*, Series 3, vol. xx.-xx., No. 23.

ON AQUEOUS SOLUTIONS OF METALLIC GOLD, AND ON THE PURPLE OF CASSIUS.

By C. L. REESE.

In a recent number of the *Annalen de Chemie* (ccci., 29), Richard Zsigmondy has published an interesting account of soluble metallic gold, obtained by reducing gold chloride in very dilute aqueous solution. The following is an abstract of his paper:—

Gold can be held in solution in water in different coloured conditions. Although the great variety of colours obtained from the colloidal silver of M. Carey Lea cannot be obtained with gold, yet gold solutions are obtained which are deep-red, blue, and black, as well as of shades lying between these colours, according to the conditions under which the gold is reduced. The blue or violet solutions seem to be the most easily obtained. The red gold solution is the one principally studied. It is obtained by treating very dilute, boiling hot, and slightly alkaline solutions of gold chloride with different reducing agents, such as formic aldehyde, acetic aldehyde, alcohol, or even hydroxylamine. Many attempts were made, with varying success, but the best conditions are the following: 25 c.c. of a solution of chlorauric acid, $AuCl_3$·HCl containing 0·6 grm. to the litre, diluted with 100 to 150 c.c. of pure distilled water, and rendered alkaline by the addition of 2 to 4 c.c. of a $\frac{3}{10}$ normal solution of potassium carbonate, are heated to boiling. As soon as the liquid begins to boil, it is removed from the flame, and 4 c.c. of a solution of 1 part of freshly distilled formic aldehyde in 100 parts of water is added gradually to the boiling-hot gold solution. In a short time the colourless liquid darkens, becomes light red, and in a few seconds attains a deep-red colour, which does not change in the slightest degree on boiling or on standing for months.

If the above directions are not strictly adhered to, not clear red, but darker purple and often violet and blue-black, turbid liquids are formed. The very dilute red solution can be evaporated to half its volume without change, but further boiling will cause it to change to a dark-violet colour, and gold will be precipitated as a black powder. The precipitation is probably due to the accumulation of salts which tend to precipitate the dissolved colloidal gold. The solution was purified by dialysis at a temperature of 40° to 50°. The solution can thus be reduced to one-twentieth of its volume in a few days, and solutions containing 0·12 per cent colloidal gold were obtained, but on further concentration metallic gold was precipitated on the parchment.

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The red gold solution passes through the closest filter-paper without change. It is tasteless. On addition of neutral salts, acids, or fixed alkalis, the beautiful red colour changes to blue; the liquid becomes turbid, gradually losing its colour, and in eight or nine hours the gold all falls to the bottom as a blue-black powder. Potassium ferrocyanide seems to act differently from other salts; it changes the colour to green, and after twenty-eight hours to pure yellow, but the gold is not precipitated. Ammonia changes neither the colour nor the solubility of the gold. The addition of an excess of alcohol changes the colour to dark-violet and precipitates the gold completely, but the precipitate, at times, retains its solubility in water.

The metallic gold in aqueous solution acts just as most other dissolved colloidal substances when subjected to electrolysis, following the negative electricity to the positive pole, where it is deposited as a black powder, which can readily be recognised as metallic gold when allowed to dry, as it immediately assumes a beautiful gold lustre. When a membrane is placed between the electrodes, the gold, like a true colloid, does not pass through the membrane, but is deposited upon it on the negative side.

Mercury does not amalgamate with dissolved gold either on being agitated with the solution or on boiling, and even when precipitated with salts amalgamation takes place very slowly and incompletely.

That the dissolved body is really metallic gold and not aurous oxide is shown by analysis of the precipitate caused by sodium chloride. The very small volume of oxygen found is undoubtedly due to air condensed on the surface of the very finely divided precipitate while drying, especially as the equivalent volume of nitrogen was also found.

When we consider the results of analysis, together with the fact that gold with metallic lustre is deposited on slow evaporation, and further that the reduction was carried out in a boiling-hot solution, and by means of a strong reducing agent, there can be no doubt that the red solution contains gold in the metallic condition.

The similarity between the colours of these solutions of gold and the colours of thin layers of gold by transmitted light is marked as well as that of red and rose ruby glass. The absorption spectra of the red solution compared with ruby glass, of the blue and violet solution with blue and violet colours of thin layers of metallic gold by transmitted light, are almost identical.

In an appendix to his paper the author referred to the fact that Faraday, in a paper on the "Experimental Relation of Gold to Light" (*Phil. Trans.*, 1857, p. 145), described many of these phenomena, and actually obtained the red solution of gold, but did not recognise it as such, attributing the colour to suspended gold in a finely divided condition.

In the same number of the *Annalen* (*Ann. Chem.*, Liebig, cccl., 361), Zsigmondy has published another article on "The Chemical Nature of the Purple of Cassius," in which the nature of this curious substance seems finally to be cleared up.

There are few substances in the field of inorganic chemistry on which so much has been done and so much written with as little result as this purple of Cassius. Up to the present time there have been two views held as to the chemical nature of this substance:—the one, that it is a mixture of stannic acid and metallic gold; and the other, that of Berzelius, that it is substantially a chemical compound of purple gold oxide with the oxides of tin, possibly mixed with an excess of stannic acid.

The solubility of the substance in ammonia favours the latter view, although Schneider lays great stress on its colloidal character, and considers the ammoniacal solution as a mixture of the "hydrosols" of gold and stannic acid.

It seemed very likely that the substance is a chemical compound of acid character, and that the solubility in ammonia is due to the formation of a salt, but it was found that by oxidation of stannous chloride, and by allowing very dilute solutions of stannic chloride to stand, the "hydrogel" of stannic acid separated out, which on the addition of a few drops of ammonia liquefied, and so became soluble in water, just as the purple of Cassius does. There can therefore be no salt formation here.

After the solutions of metallic gold in water were obtained, a substance in every way identical with the purple of Cassius was made by mixing colloidal stannic acid with colloidal gold, and precipitating with acids.

The paper is divided into three parts, the first of which is devoted to showing that the substance is not of acid character in its relation to ammonia, and to the preparation of colloidal stannic acids. This part of the work was done with J. Robitschek.

The purple of Cassius was prepared according to the method of Golfier Besseyre (*Ann. Chim. Phys.*, liv., 40), from stannous chloride solution, free from stannic chloride, and gold chloride. The washed and dried preparation was soluble neither in ammonia nor in caustic potash, but when moistened with hydrochloric acid it was easily soluble in water. When fresh and moist it is insoluble in concentrated ammonia, potassium hydroxide, or potassium carbonate, but dissolves on dilution. The ammonia solution can be boiled if left dilute so that no odour of ammonia can be detected even on addition of caustic potash, and only a trace can be detected by titration, without precipitating the substance. That the solubility in ammonia or potassium hydroxide is not due to the formation of a salt is also shown by the small percentage of these substances found on analysis—0·003 ammonia in 1 grm. and 0·4 c.c. normal alkali in 1 grm. The solubility in these reagents seems to be due to the liquefying property of the alkalis. The purple of Cassius behaves in every way like a colloid substance toward the electric current and porous membranes.

By passing a strong current of air through a very dilute solution of stannous chloride, free from gold, and allowing it to stand, it was oxidised gradually to a colloid stannic acid, which is precipitated, and, when washed free from chlorine, behaves toward reagents neither like ortho- nor meta-stannic acid. It is insoluble in strong hydrochloric acid, nitric acid, or caustic potash, but dissolves immediately on diluting to double the volume. It is soluble in water after moistening with ammonia. We have here the "hydrogel" of stannic acid which behaves toward the electric current like the purple of Cassius.

A colloidal stannic acid can also be obtained from stannic chloride when a very dilute solution of the latter (2 grms. in 3 litres) is allowed to stand for several hours. A voluminous precipitate comes down, which, when washed free from chlorine, moistened with a few drops of ammonia, and diluted, dissolves to a clear liquid which can be boiled without precipitation of stannic acid. This preparation differs from the former in that it is soluble in strong or dilute hydrochloric acid and potassium hydroxide, and not entirely in nitric acid. Potassium carbonate precipitates it from its hydrochloric acid solution, but does not dissolve it in excess.

From their properties these forms of stannic acid are seen to be neither ortho- nor meta-stannic acid; but they can be looked upon as colloidal mixtures of the two rather than individuals lying between the two, the properties of the one being hidden by those of the other. The purple of Cassius is such a mixture of gold and stannic acid hydrate, in which the stannic acid imparts to the metallic gold the property of dissolving in water by means of alkalis. This is the reason why so many chemists have for so long a time considered the substance to be a chemical compound. By mixing a solution of either of these colloidal stannic acids with a solution of colloidal gold, and precipitating by means of dilute acids or salt solutions, a gold-purple can be obtained of any

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desired composition and intensity of colour—in fact, any of a great variety of shades. The mixture does not turn blue, and then precipitate gold when treated with acids or salts, like the red gold solution, but remains unchanged even on long standing; but when boiled a red body is precipitated, which behaves, in every respect, like the purple of Cassius.

The formation of the purple of Cassius is explained by assuming that when stannous chloride is added to a sufficiently dilute solution of gold chloride, the latter is immediately reduced to metallic gold, while stannic chloride is formed. Generally after a few seconds the liquid becomes red, but the purple is not precipitated for several days unless it is heated. The gold is not precipitated as a black powder, because the stannic chloride formed is immediately hydrolysed into hydrochloric acid and the hydrate of stannic acid. The latter prevents the aggregation of the gold particles, and the stannic acid remains in solution as a colloid, which, on standing, gradually changes under the influence of the dilute hydrochloric acid to an insoluble form, the "hydrogel" of stannic acid. By heating, this change takes place immediately.

The properties of purple of Cassius depend on the properties and character of the stannic acid present, the gold playing a passive *rôle* in its relation to reagents. If the stannic acid is soluble in concentrated hydrochloric acid, so is the purple, but if it has the properties of meta-stannic acid it is insoluble in that reagent, but dissolves on distillation. In the same way the solubility in ammonia or dilute alkalis depends upon the character of the stannic acid present; in fact, the great variety in the properties of the stannic acids explains the many contradictions in the literature with reference to the properties of the purple of Cassius. Zsigmondy says, "I look upon the knowledge that a mixture of colloid bodies can behave under some conditions as a chemical compound, and that the properties of one body in such mixtures can be hidden by those in another, as the most important conclusion to be drawn from this work."

By mixing the "hydrogels" of stannic acid and silver, and precipitating with dilute sulphuric acid, a red-yellow body was obtained, which is soluble in ammonia, and a similar body was also obtained by reducing silver nitrate in the presence of a stannic acid solution.—*Amer. Chem. Journ.*, xxi., No. 2, Feb., 1899.

LONDON WATER SUPPLY.

Report on the Composition and Quality of Daily Samples of the Water Supplied to London for the Month Ending April 30th, 1899.

By SIR WILLIAM CROOKES, F.R.S.,
and
PROFESSOR DEWAR, F.R.S.

To Major-General A. De Courcy Scott, R.E.,
Water Examiner, Metropolis Water Act, 1871.

London, May 10th, 1899.

Sir,—We submit herewith, at the request of the Directors, the results of our analyses of the 168 samples of water collected by us during the past month, at the several places and on the several days indicated, from the mains of the London Water Companies taking their supply from the Thames and Lea.

In Table I. we have recorded the analyses in detail of samples, one taken daily, from April 1st to April 29th inclusive. The purity of the water, in respect to organic matter, has been determined by the Oxygen and Combustion processes; and the results of our analyses by these methods are stated in Columns XIV. to XVIII.

We have recorded in Table II. the tint of the several samples of water, as determined by the colour-meter described in previous reports.

In Table III. we have recorded the oxygen required to oxidise the organic matter in all the samples submitted to analysis.

Of the 168 samples examined by us during the month, all were found to be clear, bright, and well filtered.

The rainfall at Oxford during the month of April has been slightly in excess of the thirty years average. The actual fall was 1·83 inches; the average is 1·66 inches, giving an excess of 0·17 inch, and reducing the deficiency for the first four months of the year to 0·23 inch, or 3·1 per cent.

Our bacteriological examinations of 236 samples have given the results recorded in the following table; we have also examined 36 other samples, from special wells, standpipes, &c., making a total of 272 samples in all:—

	Microbes per c.c.
New River, unfiltered (mean of 23 samples) ..	908
New River, filtered (mean of 23 samples) ..	8
Thames, unfiltered (mean of 24 samples) ..	10622
Thames water, from the clear water wells of five Thames-derived supplies (mean of 120 samples)	22
Ditto ditto .. .. highest	185
Ditto ditto .. .. lowest	0
River Lea, unfiltered (mean of 23 samples) ..	2490
River Lea, from the East London Company's clear water well (mean of 25 samples) . ..	5

Since the beginning of the year the organic carbon in the water has been gradually diminishing, as will be seen by the following table. In spite of the excess of rain, the water during the month of April has had less soluble organic matter in solution, less colour, and its bacteriological quality has gradually improved; although at no time during the year has there been any deficiency in the effective removal of microbes by filtration.

Averages of Five Supplies derived from the River Thames.

	Common Salt. Per gall.	Hardness.	Oxygen reqd. Per gall.	Organic Carbon. Per gall.	Organic Carbon. Per gall.	Colour.
	Means.	Degrees.	Means.	Means.	Max.	Br'n: Blue.
Jan. ..	2·236	15·73	0·072	0·227	0·282	25·4 : 20
Feb. ..	2·144	15·75	0·073	0·207	0·272	26·6 : 20
March .	2·092	16·14	0·037	0·134	0·226	12·5 : 20
April ..	2·147	14·43	0·031	0·093	0·163	8·8 : 20

We are, Sir,
Your obedient Servants,
William Crookes.
James Dewar.

THE CONSTITUTION OF THE AMMONIUM-MAGNESIUM PHOSPHATE OF ANALYSIS.*

By F. A. GOOCH and MARTHA AUSTIN.

(Continued from p. 233).

In Table III. are given the results obtained in a study of the effects of varying proportions of ammonium chloride and the soluble phosphate upon the constitution of the precipitate. All precipitates were gathered upon asbestos in the filtering crucible, washed in faintly ammoniacal water, and ignited as usual. In every case the precipitation was practically complete; for, upon allowing the filtrates with the wash-water to stand for several days after further addition of microcosmic salt, nothing but insignificant traces of a precipitate—not exceeding 0·0001

* Contributions from the Kent Chemical Laboratory of Yale University. From the *American Journal of Science*, Series 4, vol. vii., No. 39, March, 1899.

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Table III.

	$Mg_2P_2O_7$ corresponding to $Mg(NO_3)_2$ taken. Grm.	$Mg_2P_2O_7$ found. Grm.	Error in terms of $Mg_2P_2O_7$. Grm.	Error in terms of MgO. Grm.	NH_4Cl present. Grm.	$HNaNH_4PO_4.4H_2O$ used. Grm.	Volume. C.m.s
			A.				
1.	0·5311	0·5418	+0·0107	+0·0038	—	2·5	150
2.	0·5311	0·5462	+0·0151	+0·0057	2	2·5	150
3.	0·5311	0·5408	+0·0097	+0·0035	2	2·5	150
4.	0·5311	0·5500	+0·0189	+0·0068	60	2·5	250
5.	0·5311	0·5520	+0·0209	+0·0075	60	2·5	250
6.	0·5311	0·5345	+0·0034	+0·0012	•	2·5	150
7.	0·5311	0·5371	+0·0060	+0·0022	•	2·5	150
8.	0·5311	0·5384	+0·0073	+0·0026	•	2·5	150
9.	0·5311	0·5386	+0·0075	+0·0027	•	2·5	150
10.	0·5311	0·5415	+0·0104	+0·0037	•	2·5	150
			B.				
11.	0·5311	0·5312	+0·0001	+0·0000	•—	2·5	150,100
12.	0·5311	0·5311	−0·0000	+0·0000	•—	2·5	150,100
13.	0·5311	0·5346	+0·0035	+0·0013	2+2	2·5	150,100
14.	0·5311	0·5348	+0·0037	+0·0014	2+2	2·5	150,100
15.	0·5311	0·5383	+0·0072	+0·0026	5+5	2·5	150,100
16.	0·5311	0·5368	+0·0057	+0·0021	5+5	2·5	150,100
17.	0·5311	0·5376	+0·0065	+0·0023	10+10	2·5	200,100
18.	0·5311	0·5395	+0·0084	+0·0030	10+10	2·5	200,100
19.	0·5311	0·5396	+0·0085	+0·0031	60+5	2·5	250,100
20.	0·5311	0·5389	+0·0078	+0·0028	60+5	2·5	250,100

Table IV.

1.	0·5311	0·5503	+0·0192	+0·0069	10	2·5	200
2.	0·5311	0·5505	+0·0194	+0·0070	10	2·5	200
3.	0·5311	0·5393	+0·0082	+0·0029	10, —	2·5	200,100
4.	0·5311	0·5351	+0·0040	+0·0017	10, —	2·5	200,100

grm.—ever appeared. In the experiments of Section A precipitations were made in the cold by the action of microcosmic salt in considerable excess upon the solutions of magnesium nitrate containing varying amounts of ammonium chloride. In Experiments 1 to 5 the liquid was made faintly ammoniacal after the addition of the precipitant, and the precipitate was filtered off immediately after complete subsidence; in Experiments 6 to 10 the precipitate first thrown down was re-dissolved in a very little hydrochloric acid and re-precipitated by dilute ammonia (the operation being repeated several times) with a view to improving the crystalline condition of the precipitate, and this treatment introduced, of course, a small amount of ammonium chloride, probably less than a grm. It will be observed that errors of excess appear in all these determinations, those being the greatest in the experiments in which the largest amounts of the ammonium salt were present.

In the experiments of Section B the manipulation was so changed that the supernatant liquid was poured off (through the filtering crucible which was to be used subsequently to collect the phosphate) after the precipitate had subsided and the insoluble phosphate was dissolved in hydrochloric acid and brought down again, after dilution, by the addition of a faint excess of dilute ammonia. By thus removing the supernatant liquid after the first precipitation, the excess of the precipitant and the amounts of ammonium chloride originally present were reduced to relatively low limits, so that their effects in the re-precipitation were at a minimum; and by adding varying amounts of ammonium chloride, or none at all, before the re-precipitation, it became possible to demonstrate the individual effect of that reagent apart from that of an excess of the microcosmic salt. It will be noted that in Experiments 11 and 12, in which no ammonium salt was added after the decantation from the first precipitate, the results are ideal, and that the errors of excess advance as the amounts of ammonium salt present in the final precipitation increase. The quantity of the ammonium salt present during the first precipitation does not influence the error in the final precipitation unless it is so large that a simple decantation of the supernatant liquid would naturally leave an appreciable amount of it to act when the second precipitation takes place.

It is plain that the errors of excess which appear when either the ammonium chloride or the soluble phosphate is present in considerable amount must be due either to mechanical inclusion on the part of the highly crystalline precipitate or to variation in the ammonium-magnesium phosphate from the ideal constitution toward a condition represented by a phosphate richer in ammonia and correspondingly deficient in magnesium. If any appreciable amount of the ammonium chloride present were held by the precipitate, it would naturally be represented by magnesium chloride after ignition, but, in no one of these experiments—even in those dealing with 60 grms. of ammonium chloride—did the residue, after dissolving in nitric acid, give with silver nitrate evidence of the presence of more than a mere unweighable trace of chloride. A special experiment, moreover, in which an attempt was made to determine the silver chloride precipitated from the solution in nitric acid of an unignited precipitate thrown down by microcosmic salt in presence of 60 grms. of ammonium chloride, confirms this conclusion; the precipitate was unweighable. If ammonium chloride present in the solution to so great an amount is not included in the precipitate in significant quantity, it would seem to be unnatural that the microcosmic salt should be included mechanically in any very great amount. But unless the microcosmic salt was mechanically included, the increase in weight must be due to the chemical influence of the reagents—that is, to the production of a phos-

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phate rich in ammonium and deficient in magnesium. Berzelius (*Jahresbericht*, 3 Jahrgang, 1824, übersetzt von C. G. Gmelin, s. 92) recognised the existence of such a phosphate of magnesium; but Wach ("Schweigger," 1830, Band 29, s. 265), in following the work of Berzelius, failed to find it. No attention seems to have been given since to the existence of such a salt. It would be natural to expect its formation, if ever, when the precipitating phosphate is in excess, and ammonium salts are present in abundance, with free ammonia. Obviously the natural effects of all these reagents would be toward the production of a salt holding more ammonia and more phosphoric pentoxide for a given amount of magnesium. The results of the table seem to point strongly to such tendencies, and, by inference, towards the existence of such a compound. Thus, in Experiments 11 and 12, in which the greater part of this excess of microcosmic salt was removed by decantation before the second precipitation, while no ammonium chloride was present excepting the small amount made by the solution and re precipitation of the first precipitate, the error is practically nothing. In Experiments 13 and 14, 15 and 16, 17 and 18, all similar to 11 and 12, excepting that ammonium chloride was present, the average errors (+0·0036 grm. in terms of magnesium phosphate, 0·0064 grm., +0·0074 respectively) increase as the ammonium chloride is increased in the final precipitation. In Experiments 19 and 20, in which the ammonium chloride amounted to 60 grms. in the first precipitation and to 5 grms. in the second, in addition to the amount that would naturally remain after decanting the strong solution of the former precipitation, the similarity of this error (+0·0082 in the mean) to that of the experiments in which smaller amounts of the ammonium chloride were used throughout goes to show that only the amount of ammonium salt present in the final precipitation counts. Further, a comparison of corresponding experiments of A and B shows very plainly that the treatment which involves the removal of the large part of the microcosmic salt, the solution of the precipitate, and re-precipitation tends to reduce the higher indications. Thus, for example, the error in 2 and 3 is +0·0124 grm. in terms of magnesium pyrophosphate, while in 13 and 14—similarly carried out, except the decantation of the excess of the precipitant, solution, and re-precipitation—the error is +0·0036 grm.

The special influence of free ammonia during precipitation was investigated in the following experiments. Definite volumes of magnesium nitrate solution were drawn from a burette into a platinum dish, ammonium chloride (10 grms.) was added, the magnesium was brought down by dilute ammonia in presence of microcosmic salt, and strong ammonia equal to one-third the volume of the solution was added. The solutions, after standing, were filtered off on asbestos under pressure in a perforated crucible, and the precipitates were washed with ammonia diluted to the proportion of three parts of water to one of ammonia, dried after moistening with a drop of saturated solution of ammonium nitrate, ignited, and weighed. The results are given in Experiments 1 and 2 of Table IV. In these determinations the mean error reaches +0·0183 grm. in terms of magnesium pyrophosphate; while in Experiments 3 and 4—made similarly, excepting that the supernatant liquid was decanted from the precipitate first thrown down, the precipitate dissolved in hydrochloric acid, and after dilution re-precipitated by dilute ammonia immediately supplemented by enough strong ammonia to make one-fourth the volume of the entire solution—the error amounts in the mean to +0·0061 in terms of the pyrophosphate.

In Experiments 1 and 2 the precipitate was influenced by an excess of microcosmic salt, ammonium chloride, and free ammonia in large amount; in Experiments 3 and 4, by decanting in the manner previously described, by dissolving the precipitate, and re-precipitating, the effects of an excess of microcosmic salt and ammonium chloride are reduced to a minimum, and, in a comparison of the results with those of Experiments 11 and 12 of Table III. the tendency of the free ammonia comes to view. The results discussed seem certainly to point to a general tendency on the part of free ammonia, ammonium chloride, and excess of the phosphate to produce a salt rich in ammonia and deficient in magnesium, which for a definite amount of magnesia precipitated must leave upon ignition a residue weighing more than the normal phosphate.

If it be assumed that a salt of the symbol $(NH_4)_4Mg(PO_4)_2$—the next natural step to the normal salt NH_4MgPO_4—is present in the precipitate, the residue which such a salt would leave upon ignition would be the metaphosphate $Mg(PO_3)_2$. From the relations of the symbols for magnesium pyrophosphate and magnesium metaphosphate, the weight of the residue obtained, and the weight of the pyrophosphate theoretically derivable from the weight of magnesium salt used, it is possible, of course, to calculate the proportionate amounts of pyrophosphate and metaphosphate present in any ignited residue. Proceeding in this manner, it appears that, in order to account for the variations noted, it is necessary to assume the presence in many cases of very considerable amounts of the metaphosphate. Thus, in the case of those results obtained according to the usually accepted method of precipitating and washing with strongly ammoniacal liquids, viz., in Experiments 1 and 2 of Table IV., the proportion of metaphosphate needed to account for the observed error reaches 10 per cent.

(To be continued).

PRESIDENTIAL ADDRESS TO THE IRON AND STEEL INSTITUTE.

By Professor Sir W. Roberts-Austen, K.C.B., D.C.L., F.R.S.

The announcement that Her Majesty the Queen will be graciously pleased to accept the Bessemer Medal for 1899, in commemoration of the progress made in the Iron and Steel Industries during Her reign, will be received with enthusiasm throughout the Empire. What the progress has been it will be my privilege to indicate in this address; for your last President of the century, in bidding it a respectful farewell, must offer the best retrospective tribute he can to the grandest industry in the world's history.

This address will, therefore, be mainly devoted to the consideration of British efforts in connection with iron and steel. I shall hope on another occasion to pay homage to the services rendered in other countries to our branch of metallurgy, but in view of our Autumn Meeting last year at Stockholm, I cannot proceed further without making a brief reference to Sweden. To her scientific men our debt is great and of long standing, for we have profited by their labours from the eighteenth century until now. We appreciated the interest in our proceedings which was shown by the presence of His Majesty the King and the Royal Princes at our meetings in the Riddarhus. The gracious kindness of His Majesty during the magnificent reception at his palace of Drottningholm will never be forgotten by those of us who were present. The spontaneous warmth of our reception by the Swedish people also touched us deeply, and the memories of our visit will be handed down as traditions to future members of our Institute, who, in the days to come, will, we trust, again seek the aid of Sweden by supplementing the ores of our own possessions with those from within the Arctic circle.

It seems strange to us now to be reminded that when the nineteenth century dawned the primitive home of the iron industry in Surrey and Sussex had not been abandoned. From my Surrey garden I look towards the tract

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once covered by the great forest of Anderida, within the bounds of which coal has recently been discovered. The survivors of the ancient trees of Andreds Wald still give shelter to a few charcoal-burners, the pursuit of whose occupation connects us with the past. There is almost within sound of me, as I write, a stream that fed one of a series of hammer-ponds, and the district within sight is believed to have furnished the coffer for the Doomsday Book, and it certainly did the iron which encircles the cathedral of our great city. The domain has further claim to remembrance, for it supplied guns for the cruisers of Drake and Frobisher. In 1740 there were four more blast-furnaces in Sussex than in any other county; in 1800 there were still two at work, and the one at Ashburnham survived until 1828, producing iron for which the claim was made that it was "in no wise inferior to the Swedish metal." These old charcoal-furnaces could rarely have exceeded 28 feet in height, with an output of some 20 tons a week. Even the greatly improved furnaces adopted about the year 1839, by John Gibbons in South Wales, did not exceed 40 feet in height. Although they were considered to be "enormous," they did not make more than 120 tons weekly. As the century closes, some of their gigantic successors, such as those possessed by our Vice-President, Mr. Andrew Carnegie, produce *daily* no less than 748 tons of iron, and much of the material which issues from them is destined to undergo complex and varied methods of treatment.

From a hill near me I can look over most of the southern home of the iron trade, and I have lingered in the reference to it because a similar comprehensive glance over the landmarks of our industry is all that time will permit me to offer you. Compared with the long past of the simple methods of extracting iron from its ore which in the South of England preceded the use of even charcoal-furnaces, the duration of modern and complex methods seems to be little more than an episode. The age of steel has not as yet endured fifty years, and tracing its rise shows that the entire history of our industry, like that of humanity, is an account of its continual changes. How did progressive development—that is, a change from the relative uniformity of primitive direct reduction processes to those of relative complexity—take place? The change is mainly due to the efforts of individuals stimulated by the country's needs. It was effected by a few men who had the courage to lay aside traditions which had been handed on for generations, and possessed the determination to make costly and laborious experiments for themselves. They were men who, being untrammelled by precedent, called in question the utility of established usages, and their endurance enabled them to solve in a new way problems of vast metallurgical importance. How could the leading British ironmasters of the first half of the nineteenth century be hindered by conventionalism when their mission was to shape the industrial life, not only of their country, but of the world? Progress was made by intellects such as our country has always had in her hours of industrial need. Both the technical workers and the experimenters in the domain of pure science were inspired by the spirit of progress, and their aim was identical. Hence the blending of efforts. Watt, Stephenson, and later Bessemer, Siemens, and others of our own body, became Fellows of the Royal Society, while a Chancellor of the University of Cambridge, and founder of the Cavendish Laboratory, was chosen as first President of the Iron and Steel Institute.

With unity of aim came diversity of method; the scientific investigator devoted himself mainly to the study of molecular problems, while the industrial worker applied his energies to dealing with iron and steel in the mass. This division of labour and unity of purpose is well maintained, and it will be my object to show how beneficial it has been and still is. At every great stage of our progress the industrial worker had an investigator of pure science close at hand.

From the technical point of view, as the eighteenth century closed, a new era in the metallurgy of iron had already begun. Abraham Darby had successfully introduced the use of coke in the blast-furnace; James Watt had, by his powerful engines, much facilitated the production of blast, and had greatly stimulated the out-turn of pig-iron. Nevertheless, the total annual production of pig-iron in the year 1799 did not exceed some 150,000 tons. From the scientific point of view the situation was one of singular interest. The early writers held that good and bad qualities might be inherent in the iron itself. Pliny points out how greatly the properties of iron depend upon its treatment, but he thought that as for the kinds of iron, they were many, and all were distinct, and the first difference arises from the diversity of the soil and climate where the mines are found. But Pliny's view survived far into the present century, and evidence of it lingered in the effective and graceful speech in which the Member for Merthyr proposed a vote of thanks to our first President on the delivery of his Inaugural Address. Mr. Fothergill said then that "thirty years ago the idea prevailed universally . . . that good iron was to be found in certain localities, and could be procured from no other place; it was found good in one place and bad in another." He adds: "Enlightened progress of the last thirty years has shown that the quality of iron depends upon the alloy with which it is mixed."

Enduring as the old view as to the influence of locality was, an experimental basis for a more accurate one had been established very shortly before the present century began, and some, at least, knew that the properties of iron depended on the presence or absence of certain other elements. This position was clearly established by the great Swedish chemist, Bergman of Upsala, who had shown that carbon is the element to which steel and cast-iron owe their distinctive properties. He had initiated the employment of calorimetric methods in determining the properties of iron and steel. He insisted that the real difficulty is to explain how it is that the presence of 0·5 per cent of carbon in iron enables the metal to be hardened by quenching from a red heat, or, in his own expressive words, *Ceterum quomodo dimidia centesima, plumbaginem efficiens, tantam provocare possit differentiam, nodus est gordius haud facile solvendus.* Bergman, moreover, anticipated the later phases of modern research by claiming that iron is a polymorphic element, and plays the part of many metals. In this early view as to the allotropy of iron it should be remembered that in 1790 our countryman, James Keir, followed him closely by urging, before the Royal Society, that what we now call passive iron "is really a distinct form of iron, the alteration being produced without the least diminution of its metallic splendour or change of colour."

Clouet's celebrated experiment on the carburisation of iron by the diamond followed. Doubts, however, were not finally set at rest until 1815, when Pepys, a working cutler in London, excluded the possibility of the intervention of furnace gas. But, as soon as the present century had well turned, the industrial world was in possession of the fundamental fact that carbon is the element of dominant importance in relation to the metallurgy of iron. Well might Bergman express astonishment at the action of carbon on iron. Startling as the statement may seem, the destinies of England throughout the century, and especially during the latter half of it, have been mainly influenced by the use of steel. Her steel rails seldom contain more than Bergman's half per cent of carbon. Her ship-plates, on which her strength as a maritime powder depends, contain less than half that amount. It is essential that the significance of this fact should be clearly understood. Our national existence has long depended on iron and steel. They have been the source of our wealth, one of the main elements of our strength, one cause of our maritime supremacy. Hardly a step of our progress or an incident of our civilisation has not, in one way or another, been influenced by the properties of iron or steel. It is remarkable that these

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properties have been determined by the relations subsisting between a mass of iron, itself protean in its nature, and the few tenths per cent of carbon it contains. These properties are, it is true, modified either by the simultaneous presence of elements other than carbon, or by the thermal or mechanical treatment of the mass. The growth of our knowledge of the facts constitutes a large section of our scientific and industrial history. The question arises—Was our national progress delayed by the unreadiness of the technical world in England to take advantage of the facts that science had established?

If we consider the position from the point of view of two remarkable men who were looking for the dawn of the nineteenth century as we are for that of the twentieth, we shall, I think, be satisfied that our progress received no check from failure of industrial workers to assimilate the teaching of science. These men were Black and Cort. Of the scientific men then living, the greatest chemist was Black, Professor at the University of Edinburgh, whom Lavoisier had generously acknowledged as his master. Black fully recognised the importance of Bergman's work, and on his own part insisted on the importance of what would now be called the change in molecular energy as the physical basis on which the properties of iron and steel depend. Black, moreover, in his public lectures gave a singularly accurate description of the process of decarburising iron called "puddling," and devised by "a Mr. Cort," with the results of whose work Black was soon to become familiar. Considering how recent the knowledge of the meaning of oxidation really was at the time, Black's statements with regard to the theory of puddling are truly remarkable. Later on he furnished the Government with an elaborate report on the quality of the material obtained by puddling. He showed, by such mechanical tests as the experience of the time suggested, the superiority of puddled iron, and pointed out that it was more suitable than foreign iron for the appliances "on which," as he says, "the lives of our seamen and the safety of our ships have hitherto mainly depended."

1799. At the end of the century we are justly proud of our Colonial possessions, and are satisfied that the varied applications of iron and steel will enable us to knit together all parts of the Empire. At the beginning of the century Lord Sheffield, in his "Observations on the Commerce of the American States," writing in the early days of Cort's process, shows that it would help to make British iron as cheap as the foreign, an event which he considered would be more advantageous to England than the possession of her American colonies. Black died in 1799, Cort survived till 1800, so that, as the eighteenth century closed, the most eminent scientific man and the foremost practical metallurgist of the generation stood side by side. To Cort we owe the greatest technical advance the modern world had seen; to Black, the recognition of the importance of molecular energy in relation to metallurgical problems.

1800. The production of pig-iron in this country also received a great stimulus from the discovery by Mushet, about the year 1800, that the large deposits of blackband ironstone could be utilised. The century opened with, in round numbers, an annual production of pig-iron not exceeding 200,000 tons, of which less than one-third was converted into bars and other descriptions of wrought-iron. The capital invested was under five millions, and employment was furnished for nearly 200,000 people.

1803. Returning to the scientific aspect disclosed at the dawn of the century, the year 1803 was an eventful one for science. Nevertheless the impulse given to research was not in the most favourable direction for the advancement of metallurgic art. The influence of a small proportion of carbon on iron had been recognised, but the quantitative relation between the iron and the carbon was only considered as bearing on the nature of the product, and not at all from the point of view of chemical union. When, therefore, in 1803, Claude Louis Berthollet published his "Essai de Statique Chimique," it appeared that the action, of what for the moment I may be permitted to classify as the action of *traces* upon *masses*, was in a fair way to be elucidated for the following reason:—Berthollet pointed out that "in comparing the action of bodies on each other which depends on their affinities and mutual proportions, the influence of mass has to be considered." Unfortunately in succeeding years the views of Prout, the courteous opponent of Berthollet, prevailed, mainly through the powerful aid of Dalton, who published also in 1803 his first table of atomic weights. Hence the phenomena which could not be attributed to fixed atomic proportions were set aside and usually neglected. Evidently the action of one-tenth per cent of carbon on iron could not be explained by the aid of combining weights. The century was more than half over before a school of eminent chemists arose, who did not insist that matter is minutely granular, but in all cases of change of state made calculations on the basis of work done, viewing internal energy as a quantity which should reappear when the system returns to its initial state.

1802-7. The production of cast-iron and bar-iron was rapidly increasing, and the suitability of cast-iron and bar-iron for the construction of bridges became evident to engineers, among whom Telford was pre-eminent. A distinguished professor, a worker in pure science, came, in the person of Dr. Thomas Young, to the aid of the technical worker. The need of studying the mechanical properties of iron and steel was evident, and Young showed that the work done in permanently extending or in compressing iron or steel could be represented by a coefficient, to which he gave the name of the "Modulus of Elasticity." This coefficient has probably rendered more service in the development of the study of the strength of iron and steel than any other which has been determined. It is of great importance, because upon it depends the deflection which a structure will take under strain. Young, evidently with a view to bring home evidence as to the great rigidity of steel, gives in his original paper a quaint illustration. He therein shows that if "Hook's law holds" a hanging rod of steel would have to be 1500 miles long in order that the upper portions of it might be stretched to twice their original length. I would incidentally point out that, on the basis of Young's calculation, such a column 1500 miles high, if it were 1 ft. $2\frac{1}{16}$ inches in diameter, would represent the output for the past year of Bessemer steel in this country alone. Statements of this kind had such a singular fascination for Sir Henry, that I have permitted myself a brief departure from chronological order in offering this one.

1817. In the year 1817 the patent was granted to the Rev. Robert Stirling, the specifications of which showed that he had a clear conception of the "regenerative principle," which, applied to furnaces, as will be shown later, has been so fruitful in connection with the manufacture of steel.

1818. In the year 1818, Samuel Baldwin Rogers substituted "iron bottoms" for the sand ones which had been introduced by Cort in the puddling-furnace. I find in the work on "Iron Metallurgy" by Rogers, published in 1857 (but apparently embodying much information he had promulgated in 1818), the statement that his "principal aim" in proposing the use of iron bottoms for puddling-furnaces was "to work the iron in a bath of cinder." He also suggested the use of a flux of a very basic character, and he adds the very interesting statement that use of "the proposed flux will rapidly remove the metalloids from the iron." He pointed out that "the metalloids were removed in the shape of oxides, and combined with the cinder in the puddling-furnace." The actual result was to greatly improve the quality of British iron, and therefore Rogers deserves recognition, which has hardly been accorded to him, as a pioneer of the great basic process of dephosphorisation.

Between the years 1800-4 the amount of foreign iron annually imported was 40,200 tons, and one consequence

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of the improved method of puddling was to greatly diminish the importations, which in the period 1823 to 1830 fell to 17,015 tons a year.

1820. In the year 1820 malleable iron began to replace wood for the manufacture of colliery rails, mainly through the efforts of Birkenshaw.

The first quarter of the century did not draw to an uneventful close, for Faraday, working with Stodart, an eminently practical man, gave (in 1820) a stimulus to the study of alloys, and produced the first specimen of nickel steel. In a letter to De la Rive dated April 20, 1820, Faraday writes:—"Mr. Stodart and myself have been engaged in a long series of experiments and trials on steel, with the hope of improving it, and I think we shall in some degree succeed." Later on he writes:—"If you knew the labour of the experiments you would applaud us for our perseverance at least."

1822. In the year 1822 Faraday pointed to a fundamental difference between hard and soft steel, the latter yielding a "carburet of iron" when treated with hydrochloric acid, while hardened steel dissolves completely.

1828. Early in the second quarter of the century notable progress was made, for on the 3rd of March, 1828, James Beaumont Neilson enrolled his patent for the application of the hot-blast to furnaces. It has been suggested by two of my predecessors in this chair that the introduction of the hot-blast might be characterised as a "lucky hit." Viewing, however, the merits of Neilson's great invention in relation to general metallurgical progress, it will be evident that exception may be taken to this suggestion. Neilson's contemporary, David Mushet, held that the introduction of the hot-blast "marked one of the grandest epochs in the history of the manufacture of iron," and he urged that the discovery was the more remarkable as being opposed to received opinions and prejudices, "it being universally held that the blast should be kept as cold as possible." Neilson was an enthusiastic student in Anderson's College, Glasgow, and his strenuous advocacy of technical instruction proved him to be singularly in advance of his age; he was also an ardent experimenter. Moreover, he clearly says he was led to think that "if air was increased in volume by heat, it might be enabled to do more duty." In a sense he was right, for the expansion of the air, though perhaps it was not so important as he thought, represents one-third of the energy contributed by the intervention of the hot-blast stove. That his invention owed anything to "luck" was evidently not the opinion of our own Royal Society, of which body he was elected a Fellow in 1846, as the discoverer of the "hot-blast system of manufacturing iron," and as being "distinguished for his acquaintance with the science of mechanical philosophy." The practical results of the hot-blast were marked, and in the ten years which followed the introduction of his invention the production of pig-iron in this country was more than doubled. The history of the period is singularly interesting.

1842. A patent of June 9, 1842, embodies the first drawing of the perfected single-acting steam-hammer. Such hammers had been proposed by James Watt in 1784, and sketched by Deverell in nearly its present form in 1806.

1843-48. At this time a great investigator appeared in the person of Dr. Thomas Andrews of Belfast, the application of whose great work on the heat of combination will be referred to later.

(To be continued).

Formation of Alums by Electrolysis.—Jas. Lewis Howe and E. A. O'Neal.—Solutions of metals in the lower state of oxidation were electrolysed in a platinum dish, which formed the positive electrode, in presence of sulphuric acid and the different alkali sulphates. The rubidium and cæsium iron alums and the rubidium and cæsium cobalt alums were prepared in this way.—*Journ. Am. Chem. Soc.*

NOTICES OF BOOKS.

Liquid Air and the Liquefaction of Gases. History, Theory, Biography, Practical Applications, Manufacture. By T. O'Conor Sloane. Illustrated. New York: Norman W. Henley and Co. 1899. Pp. 365, 12 mo.

This timely work aims to tell the history of the liquefaction of gases during the last century, and treats the subject from the biographical as well as the scientific standpoint. The author is already known by his works "Electricity Simplified," "How to Become a Successful Electrician," "Electric Toy Making," and the more voluminous "Standard Electrical Dictionary," which has passed to a second edition.

In the book under review Dr. Sloane explains in simple language the fundamental facts of the physics of gases, the measurement of heat by divers kinds of thermometers, the relations of heat to gases, and the physics and chemistry of the air; he then takes up the experimental researches on the liquefaction of gases made by Faraday, and all his successors to the present time. Dealing with the subject historically he introduces in their proper place a notice of the Royal Institution, and biographical sketches of those who have successively held the chair of chemistry therein, from Davy to Dewar. The contributions of Northmore, Cagniard de la Tour, Colladon, Thilorier, Natterer, and Andrews to the liquefaction of gases, are duly explained, and the divers forms of apparatus are shown in illustrations. The writer of this review knows of no work or treatise that contains so full and accurate accounts of the lives and services of Raoul Pictet, Louis Paul Cailletet, Sigmond von Wroblewski, Karl Olszewski, James Dewar, and the American inventor Charles E. Tripler. Dr. Sloane remarks in the preface that the "personal friendship of that wonderfully endowed scientist, Raoul Pictet, one of the fathers of liquid air, poet, musician, physicist, chemist and mathematician, a veritable Admiral Crichton," brought about by writing the book, fully justified the labour bestowed upon it. The volume contains good portraits of Faraday, Pictet, Cailletet, Dewar, and Tripler. Of the latter Dr. Sloane writes: "While Dewar, working on the lines laid down years before by Pictet and assisted by liberal gifts from one of the London Guilds and from private individuals, liquefied gases at great expense, here in the metropolis of the United States, a private individual has erected a plant at his own expense, and for years has liquefied air on a scale which Dewar and his associates never dreamed of. In order to preserve liquid air Dewar devised his celebrated vacuum bulb, an apparatus of the highest merit. Tripler took common tin cans, lined them with felt, filled them with two to five gallons of liquid air, and sent them off hundreds of miles by rail." Linde, with his peculiar apparatus, secured three quarts of liquid air per hour, in May, 1895. Dr. Hampson's apparatus is said to work on the same lines as that of Linde.

Chapter xvii. is devoted to Pictet's experiments in frigotherapy; he found that immersion of his body for eight minutes in a well reduced to the temperature of −110° C. (−166° F.) cured him of long standing dyspepsia. Dr. Fish Clark, of New York, has removed cancer, bunions, corns, warts, and superfluous hair by the application of solid carbon dioxide. The author reviews the applications of liquid air to industrial uses, as an explosive, in electric power work and as a reservoir of energy.

The volume can be recommended to all interested in the wonderful progress of our knowledge of the physics and chemistry of gases. It is pleasantly written, but the author sometimes repeats himself, a blemish to be eliminated in a second edition. Owing to carelessness of the printer and publisher the running head lines of the 365 pages do not change, whereas each chapter should have given to the pages an independent head-line. This defect is by no means peculiar to Dr. Sloane's excellent volume, nor can it be said to detract from its scientific value.

H. C. B.

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Notes on Volumetric Analysis. By Arthur Thornton, M.A., and Marchant Pearson, B.A. London, New York, and Bombay: Longmans, Green, and Co. 1898. Pp. 80.

Volumetric analysis is a most important branch of quantitative chemical analysis; by its means the speed and number of estimations has been enormously increased, and it also affords the student practice in careful manipulation and accurate observation, while at the same time exercising the reasoning faculties. A volumetric experiment can be divided into three sections:—I., *The Principle*, explaining the nature of the reaction and the method of making the solutions; II., *The Method*, which gives full instructions how to conduct the experiment; and III., *The Record*, which gives a clear statement of the numerical details and of the simple mathematics involved in the problem, the last point being one of considerable importance, as it is frequently found that students can perform the chemical experiment accurately, but cannot work out the results through want of mathematical skill.

The experiments described fully illustrate all the simple processes of neutralisation, oxidation, and iodometry. There is also a short chapter on precipitation methods, such as the use of nitrate of silver.

The book will be found of great practical use, not only to students, but as a laboratory companion.

New York Experimental Agricultural Station, Geneva, N.Y. Report of Analyses of Commercial Fertilisers for the Spring of 1898. No. 145. By L. L. Van Slyke. Published by the Station. 1898.

During the spring of 1898, 1183 samples of commercial fertilisers, representing 739 different brands, were collected; of these 578 were complete, while certain numbers of the others contained either nitrogen, phosphoric acid, or potash only, or two of these ingredients without the third.

The nitrogen present in the complete fertilisers varied from 0·12 to 8·21 per cent, averaging 2·20 per cent. The average amount found by the Station exceeded the amount guaranteed by 0·16 per cent; the greatest excess was 3·27 per cent.

The available phosphoric acid found varied from 3·69 to 14·28 per cent, and averaged 8·65 per cent. The amount of phosphoric acid soluble in water varied from 0·10 to 11·11 per cent, and averaged 5·08 per cent.

The potash present in the complete fertilisers varied from 0·22 to 15·22 per cent, and averaged 4·91 per cent. In 426 brands of these fertilisers the amount of potash present was above that guaranteed, and in 140 brands it was below. In 110 cases the potash was present as sulphate free from excess of chlorides.

CORRESPONDENCE.

THE 32 EQUIVALENT AND ITS RELATION TO THE PERCENTAGE OF AVAILABLE SODA IN CAUSTIC SODA.

To the Editor of the Chemical News.

Sir,—In his letter in the Chemical News of May 19th (vol. lxxix., p. 239) Mr. Hooper says:—"Mr. Pattinson states in his letter that the test-acid on the 32 equivalent is weaker than *the true normal acid.*"

I beg to point out that I did not use the words in italics. I did say, however, "English test-acid is weaker than test-acid made on the correct equivalent of soda," and this statement requires some explanation. Before the use of French weights and measures had become general in laboratories in this country, it was customary in laboratories of alkali works on the Tyne to make the test-acid of such a strength that 592·5 fluid grains, or 59·25 measures on a burette exactly neutralised 50 grains of pure carbonate of soda. With this test acid, the reading of the burette indicated the percentage of soda in a sample when 50 grains of it were operated upon. Now, 50 grains of pure carbonate of soda neutralised by acid made in a similar way, but on the basis of the 31 equivalent of soda, requires only 58·49 measures of such acid. The English test-acid made in this way on the 32 equivalent is therefore weaker than the acid similarly made on the 31 equivalent. As I did not explain in my previous letter how the test-acid used to be made, I think Mr. Hooper is to be excused for having misunderstood me.

Mr. Hooper, however, still does not see that my tables quoted and extended by Dr. Lunge are quite correct. They do just what they profess to do—viz., give the equivalent in English alkalimetrical degrees of any real percentage of soda. In other words, they state what the test would be if actually made with English test-acid.

Mr. Hooper makes some calculations based on the assumption that "a normal acid which saturates 54 parts of Na_2CO_3 *will neutralise* 41 *parts NaHO or* 32 *parts* Na_2O." He will see that this assumption is wrong if he considers the amount of sulphuric acid in a normal acid that saturates 54 parts Na_2CO_3. Such an acid contains 49·924 grms. H_2SO_4 per litre, and will saturate 54 grms. of Na_2CO_3, or 40·75 grms. (not 41 grms.) of NaOH, or 31·585 grms. (not 32 grms.) of Na_2O. One c.c. of it is therefore equivalent to 0·054 grm. Na_2CO_3, 0·04075 grm. NaOH, or 0·031585 grm. Na_2O. 4·1 grms. of caustic soda therefore require for neutralisation, *not* 100 *c.c.*, but $\frac{4{\cdot}1 \times 100}{4{\cdot}0} = 100{\cdot}61$ c.c.; or stated in terms of soda, Na_2O, 3·2 grms. of caustic soda would require $\frac{100{\cdot}61 \times 3{\cdot}2}{4{\cdot}1} =$ 78·52 c.c.; that is to say, pure caustic soda actually containing 77·5 per cent of soda will, when tested with English test-acid, indicate 78·52 English alkalimetrical degrees of soda.

If Mr. Hooper will only make some English test-acid as prescribed by Dr. Lunge and test some caustic soda with it, he will prove experimentally that the tables are quite correct.—I am, &c.,

John Pattinson.

75, The Side, Newcastle-upon-Tyne,
May 24, 1899.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

Note.—All degrees of temperature are Centigrade unless otherwise expressed.

Berichte der Deutschen Chemischen Gesellschaft.
Vol. xxxi., July 11, 1898.

Research on Optical Activity.—L. Tschugaeff.—The author has studied the variations in the rotatory power of the homologous series, principally of the aromatic ethers of menthol.

Presence of Di-isopropyl in the Ether of Baku Petroleum.—O. Aschan.—Already noticed.

On the Acetals of Acrolein and of Glyceric Aldehyde.—A. Wohl.—Acetal of chloropropionic aldehyde is easily obtained by saturating two volumes of cold absolute alcohol—to which is added, little by little, one volume of acrolein, with hydrochloric acid gas. It separates in the form of a heavy oil, which is treated with dry bicarbonate of soda, washed with water, and dried over K_2CO_3. One part of this raw acetal has then added to it two parts of powdered

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KOH, and the whole is distilled between 125° and 130°; the distillate is fractionated a second time, and is then practically pure acetal of acrolein, $CH_2=CH.CH(OC_2H_5)_2$. It is in the form of a mobile liquid, having an agreeable odour, slightly soluble in water, and boiling at 125·5°. The acetal of glyceric aldehyde is prepared by heating the acetal of oxychloropropionic aldehyde for several hours with an aqueous solution of K_2CO_3, or by oxidising acetal of acrolein in suspension in water by $KMnO_4$ at 10 per cent in the cold, 2—3°. Solid K_2CO_3 is added to the filtrate, the acetal is isolated by means of ether, and purified by distillation in vacuo.

The Isomeric Chlorides of *o*-Sulphobenzoic Acid, and on an Interesting Case of Tautometry.—R. List and M. Stein.—The authors undertook this investigation before the publication of M. Remsen's results, and, as far as concerns dissymmetry, they have obtained very different results, as shown in this paper. The chlorides in question each react as if they were tautomers, and, further, they cannot be transformed one into the other. The one melting at 79° reacts less easily than the one melting at 40°; thus the author has called them respectively the stable and instable chlorides.

Condensation of Salicylic Aldehyde with the Acid Amides.— F. Cebrian.— Salicylic aldehyde condenses with the acid amides with elimination of water: $C_6H_4<^{OH}_{CHO} + R.CO.NH_2 = C_8H_6O_2NR + H_2O$. Acetamide, formamide, and benzamide act the best. The products of condensation are amorphous powders, not very soluble as a rule except in cold dilute alkalis.

The Semicarbazone of α-Ionone.—F. Tiemann.—The product of the action of H_2SO_4 on pseudo-ionone contains a mixture of pseudo-ionone, ionone α, and ionone β. This mixture is heated with alcoholic KOH, to decompose the uncondensed pseudo-ionone. The two isomeric ionones are then caught by a current of steam and transformed into semicarbazones by means of the chlorhydrate of semicarbazide and acetate of sodium. The mixture of the two semicarbazones is crystallised several times in absolute alcohol; the first portions consist of pure semicarbazone of β-ionone. The mother-liquors are treated with H_2SO_4, then by hydrochlorate of hydroxylamine; the oxime α which is deposited is decomposed by an acid, and the ionone α regenerated in a state of purity. The semicarbazone of α-ionone melts at 138° after several crystallisations in dilute alcohol.

On the Derived Bases of Xylylene-diamine, and on a Nucleus with Eleven Links.—M. Scholtz.—The action of NH_3 at a high temperature on quaternary bromides causes the replacement of the bromine by the NH_2 group, and the simultaneous migration of one of the alcoholic radicals, thus—

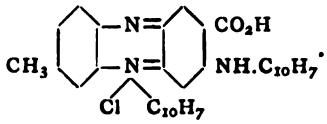
$$C_6H_4<^{CH_2}_{CH_2}>^{N}_{Br}<^{R}_{R'} + NH_3 = C_6H_4<^{CH_2-NH.R}_{CH_2-NH.R'} + HBr.$$

This reaction takes place even when the secondary amine, $NH<^{R}_{R''}$, is a cyclic base, such as piperidine.

The Use of Bromide of *o*-Xylylene for Detecting the Bases.—M. Scholtz.—A continuation of the research on the action of bromide of *o*-xylylene on the primary, secondary, and tertiary fatty and aromatic amines. The author divides the amines into eight groups, which are here described.

Nitrophenols derived from the Bromoparatoluidine of Wroblewski [$C_6H_3Br(CH_3).NH_2$. 1 : 2 : 3].—J. T. Hewitt and H. E. Stevenson.—The authors describe the preparation and properties of bromotolunitrophenol, bromotolunitro-α-naphthol, and bromotolunitrosalicylic acid.

The Action of α-Naphthylamine on Bromo-tolunitrosalicylic Acid.—J. T. Hewitt and H. E. Stevenson.—By the action of α-naphthylamine on bromotolunitrosalicylic acid an atom of bromine is separated, and a difficultly purified halogen body is formed. This is dissolved in alcoholic KOH, then precipitated with water. The acetic solution of this precipitate is treated with concentrated hydrochloric acid, and a crystalline hydrochlorate is obtained, having a violet colour, and answering to the formula $C_{34}H_{24}ClN_3O_2$. The energy with which the acid is combined in this substance points to the following constitution:—



The corresponding base has not been isolated, but its different salts—bromide, iodide, nitrate, sulphate—have been obtained; they are insoluble in water.

Note on Nitrophenine.—J. T. Hewitt and H. E. Stevenson.—The authors consider that the symmetric formula given to this body by Fischer and Hepp is inadmissible. This is confirmed by a direct experiment with hydrazophenine. The denitration of this body gives a negative result. Hydrazophenine does not contain a primary amine group.

Physico-chemical Study of the Salts of Diazonium. Hydrate of Diazonium and the Normal Diazoïcs.—W. B. Davidson and A. Hantzsch.—The authors have made a large number of determinations of electrical conductivity and heats of neutralisation, and have succeeded in showing that in its salts diazonium behaves like ammonium, while the hydrate of dinitrobenzene, treated with an alkali, gives off a quantity of heat, such as would be afforded by a strong acid under the same conditions.

On the Action at a Distance of Substituted Groupings in the Tetrazolium Nucleus.—E. Wedekind and L. Strauwe.—The authors have made a comparative study of a series of formazoylic derivatives,—

$$R.C<^{N-NH.X}_{N-N\ .\ Y'}$$

with the object of establishing the influence of the groups R, *x*, and *y* on the facility of oxidation of these compounds. The group R has far the greater influence.

Journal de Pharmacie et de Chimie, Series 6, Vol. ix., No. 3.

On Anabsinthine: a New Substance derived from Absinth.—MM. Adrian and Trillat.—This substance is prepared by making successive alcoholic extracts of the plant; these are evaporated down, and after a preliminary filtration a chloroformic extract is made. This extract is dissolved in boiling alcohol, and the organic matter precipitated with acetate of lead, until no further precipitate is formed; filter cold, and add tartaric acid to remove the excess of lead salt, and filter again. The extract resulting from the complete evaporation of the alcohol is washed with water until no longer acid; dry, and when warm add one part of rectified benzene. On cooling we obtain, after some days, a crystalline mass, which is left to drain, and washed with cold benzene. This is dissolved again in boiling alcohol, and, on the addition of a little water, the crystals again appear at the end of half-an-hour. These crystals are anabsinthine; they take the form of long, white, prismatic needles. The formula given to this product is $C_{18}H_4O_4$; this formula has been confirmed by cryoscopic means. If dried at 120°, the fusing-point of anabsinthine is 258—259°; after being exposed to the air, this falls to 236—238°: it is slightly soluble in water, and more so in alcohol, benzine, and chloroform. It crystallises in acetone in magnificent crystals, the facets of which may reach 1 c.m. in width—a veritable crystallographic curiosity.

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MISCELLANEOUS.

Opening of the Dronfield Sewage Works.—The new sewage disposal works of the Dronfield Urban District Council recently opened, have been completed in accordance with the design of the Council's engineer, Mr. G. White, C.E., of Mexboro', and are on the international system, comprising Candy circular upward flow tanks with automatic sludge or detritus removal apparatus, clarifiers, and polarite oxidising filter-beds—now popularly termed bacteria beds. The scheme has been carried out in accordance with the plans approved by the Local Government Board, the contractors being Messrs. Margerrison and Sons, of Dronfield.

Purdue University.—This University embraces six departments of instruction, the courses of each extending through four years. They are Mechanical, Civil, and Electrical Engineering, Applied Sciences, Agriculture, and Pharmacy. In addition to the regular instruction there will now be given a series of lectures on different departments in the organisation of railways. American railways are entering upon a period of development, the conditions of which are more exacting than any they have hitherto experienced. The volume of traffic is increasing enormously, and increased speed is constantly demanded; this necessitates more and more attention to the question of safety, and therefore a demand for men who are thoroughly trained for the service. Purdue University has for several years offered work covering a considerable variety of railway subjects, but recently the plan has been revised, new subjects added, and consequently a department of railway engineering and management formed.

Royal Institution.—An adjourned General Meeting of the Members of the Royal Institution was held on the 22nd inst., His Grace the Duke of Northumberland, President, presiding, when the following foreign scientific men were elected Honorary Members, in commemoration of the Centenary of the Royal Institution, which will be celebrated on the 5th, 6th, and 7th of June next:—Professor S. Arrhenius (Stockholm), Professor C. Barus (Brown University), Professor H. Becquerel (Paris), Professor G. L. Ciamician (Bologna), Professor N. Egorof (St. Petersburg), Professor A. P. N. Franchimont (Leiden), Professor A. E. Gautier (Paris), Professor H. G. Kayser (Bonn), Professor W. Körner (Milan), Mr. S. P. Langley (Washington), Professor G. L. Van der Mensbrugge (Ghent), Professor A. A. Michelson (Chicago), Professor H. Moissan (Paris), Professor R. Nasini (Padova), Professor W. Nernst (Göttingen), Professor W. Ostwald (Leipzig), Dr. E. Solvay (Brussels), Professor R. Thurston (Cornell), Professor E. Villari (Naples), Professor J. L. G. Violle (Paris), Dr. E. Ador (Geneva), Dr. L. Bleekrode (The Hague), Professor J. S. Ames (Johns Hopkins University), Professor G. F. Barker (Philadelphia), Dr. O. Liebreich (Berlin), Dr. W. L. Wilson (Washington).

New Method of Detecting and Estimating Acetone in Water, and in the Methylic and Ethylic Alcohols.—G. Denigès.—To detect acetone in—(A) *Aqueous solution*, 2 c.c. must be mixed with 2 c.c. of a mercuric reagent (dissolve 5 grms. of mercuric oxide in a hot mixture of 20 c.c. of sulphuric acid and 100 c.c. of water); plunge into boiling water; if after ten minutes' boiling there is no cloudiness or precipitate, acetone is not present; if, on the contrary, acetone is present, the amount of precipitate or cloudiness is in proportion to the amount of acetone: the precipitate, however, is never seen in less than forty-five seconds. In (B) *Methylic solution*, proceed as before, but add 2 c.c. of methylic alcohol, 2 c.c. of water, and 4 c.c. of mercury reagent; this must be diluted with water, as the undiluted methylic alcohol when heated precipitates the mercuric sulphate: by this process we can detect 3 centigrms. per litre of the original solution. (C) *Ethylic solutions.*—In the case of ethylic alcohol we must have such a dilution that the alcoholic degree of the liquid shall not be more than 2, or else the mercurous sulphate arising from the reducing action of the alcohol will be precipitated on boiling. Thus a solution of acetone in ethylic alcohol at 90° should be diluted to one-fiftieth, and then treated in the same manner as the aqueous solution.—*Journ. de Pharm. et de Chimie*, Series 6, vol. ix., No. 1.

MEETINGS FOR THE WEEK.

TUESDAY, 30th.—Royal Institution, 3. "Recent Advances in Geology," by Prof. W. J. Sollas, D.Sc., F.R.S.
—— Society of Arts, 8. "The Revival of Tradesmen's Signs," by J. Starkie Gardner.
THURSDAY, June 1st.—Royal Institution, 3. "Water Weeds," by L. C. Miall, F.R.S.
—— Chemical, 8. "The Hydrosulphides, Sulphides, and Polysulphides of Potassium and Sodium," by W. Popplewell Bloxam. "On the Relative Efficiency of various Forms of Still-head for Fractional Distillation," by Sydney Young, D.Sc., F.R.S. "The Salts of Dimethylpyrone, and the Tetravalence of Oxygen," by J. N. Collie, Ph.D., F.R.S., and Thomas Tickle.
—— Society of Arts, 4.30. "The Port of Calcutta," by Sir Charles Cecil Stevens.
SATURDAY, 3rd.—Royal Institution, 3. "The Music of India and the East, and its Influence on the Music of Europe" (with Musical Illustrations), by Edgar F. Jacques.

REDRUTH SCHOOL OF MINES, CORNWALL.

Principal and Instructor in Inorganic Chemistry, Assaying, and Mineralogy	Mr. J. PAUL DE CASTRO. B.A. (Cantab.), F.C.S.
Mining, Ore Dressing, and Geology	Mr. THOMAS COLLINS.
Panning, Vanning, Rock Drilling, and Timber Cutting	Capt. W. HAMBLY (late H.M. Inspector in S. Africa).
Mine and Land Surveying	Capt. F. WICKETT (Bassett Mines, Ltd.).
Steam, Machine Construction, and Applied Mechanics	Mr. J. C. KEAST.
Mathematics	Mr. F. R. PASCOE, B.A. (Lond.) Mr. H. E. RUSSELL, B.A. (Dublin).

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THE CHEMICAL NEWS.

Vol. LXXIX., No. 2062.

ON A TUNGSTO-LITHIC TUNGSTATE.

By L. A. HALLOPEAU.

I have already shown in a previous paper (*Bull. Soc. Chim.*, Series 3, vol. xix., p. 746) that hydrogen reduces the alkaline paratungstates at a red heat. With the paratungstates of sodium and potassium we obtain tungsto-sodic and tungsto-potassic compounds—or, as they were formerly called, *tungsten bronzes*. The paratungstate of lithium is reduced more completely and binoxide of tungsten is abundantly formed.

To obtain tungsten bronze with the paratungstate of lithium it is necessary to make this salt react on a reducing agent other than hydrogen.

Scheibler announced the production of quadrangular blue tablets by the action of tin on melted tungstate of lithium. Long afterwards, von Knorre took up the subject. He stated that this blue compound might *perhaps* contain $Li_2W_5O_{15}$.

As all this was not very decisive, I undertook to repeat this experiment and make a careful analysis of the product of the reaction.

Paratungstate of lithium was heated for an hour with a small quantity of tin. The operation was carried out in a porcelain crucible placed in a muffle furnace and heated to bright redness. The melted mass was treated successively with boiling water, concentrated hydrochloric acid, and a boiling solution of lithia at about 20 per cent. After a final washing with warm water, a powder remains, having a very deep blue colour and composed of microscopic prisms. The blue coloration is very intense when the product is freshly made, but it eventually assumes a slightly greyish appearance.

The analysis I made of this substance confirmed the formula $Li_2W_5O_{15}$, which may also be written thus:—$Li_2O,WO_3+WO_2,3WO_3$.

	Found.	Calculated.
Li_2O	2·55	2·56
5W	78·19	78·36
14O	—	19·08
		100·00

From its constitution this body resembles tungsten bronze, $Na_2O,WO_3 + WO_2,3WO_3$, which is also prismatic, and which has been obtained by Philipp by melting an acid tungstate of sodium with tin.—*Bull. Soc. Chim.*, Series 3, vol. xx.-xx., No. 23.

ON THE COMPOSITION OF THE OSMIAMATES.

By L. BRIZARD.

In the year 1847, Fritzsche and Struve (*Bull. de l'Acad. de St. Petersbourg*, vol. vi., p. 81) described the salts of an osmium compound containing nitrogen and oxygen, to which they gave the name osmiamic acid. The analysis of osmiamate of potassium led them to assign to it the formula $Os_2N_2O_5K_2$.

In 1891, M. Joly (*Comptes Rendus*, vol. cxii., p. 1442) took up the study of these compounds. He examined particularly the conditions of the preparation of osmiamate of potassium and the products of its decomposition by heat, and he came to the conclusion that the formula given by Fritzsche and Struve ought to be modified and replaced by $OsNO_3K$. Osmiamic acid would therefore have the formula $OsNO_3H$, and might be considered as the first anhydride of a body $OsNO(OH)_3$ entirely analogous to the hydrate, $RuNO(OH)_3$, already examined by M. Joly. Osmiamic acid and the osmiamates would thus be nitroso-compounds of osmium.

The estimation of the osmium in osmiamate of potash would have removed all doubts, but M. Joly decided to attempt this later on. This estimation, in fact, presents a certain difficulty; it is impossible to use the ordinary method of analysis, which consists of first reducing the material in a current of hydrogen and then isolating the reduced metal by washing with water. In actual practice the osmium remains mixed with the alkali and we cannot effect its separation by means of water, as a part of the metal becomes transformed into a volatile peroxide.

Having undertaken the examination of the action of reducing agents on the nitroso-compounds of the platinum metals, I found it necessary to verify, by a complete analysis, M. Joly's statements on the composition of the osmiamates.

Osmiamate of Potassium.—I prepared this salt by the method given by Fritzsche and Struve, viz., the action of ammonia on a solution of peroxide of osmium in potash, taking the exact proportions shown by the formula $OsO_4+KOH+NH_3=OSNO_3K+2H_2O$. To estimate the osmium, I first precipitated it from the solution of the osmiamate in the state of sulphide, taking the precautions recommended by M. Lecoq de Boisbaudran (*Comptes Rendus*, vol. xcvi., p. 1838), so as to obtain complete precipitation. The osmium is thus separated from the alkali. The reduction of the sulphide obtained by means of a current of hydrogen leaves only osmium as a residue.

I estimated the potassium by reducing the osmiamate in a current of hydrogen, separating the alkali from the osmium by washing with water and then transforming it into chloride of potassium. These analyses gave me the following results:—

	Found.			Calculated.	
	I.	II.	III.	Fritzsche and Struve.	Joly.
Os	65·1	65·2	—	67·1	65·3
K	—	—	13·33	13·76	13·38

Osmiamate of Ammonium.—I prepared this body by the action of osmiamate of silver on a solution of chloride of ammonium. The solution of osmiamate of ammonium thus obtained is sufficiently stable to remain exposed in dry vacuo at the ordinary temperature for several days; it then gives very beautiful crystals, isomorphous with those of the potassium salt (H. Dufet, *Bull. Soc. Min.*, vol. xiv., p. 214; and vol. xviii., p. 419). The reduction of this salt in a current of hydrogen leaves a residue of pure osmium, which can be easily weighed. I have also estimated the ammonia present by Schlœsing's method, and found:—

	Found.		Calculated.	
	I.	II.	Fritzsche and Struve.	Joly.
Os	70·2	—	72·5	70·4
NH_3.. ..	—	6·0	6·4	6·2

Osmiamate of Silver.—This salt, slightly soluble in water, is deposited immediately when we treat a solution of osmiamate of potassium with nitrate of silver at the ordinary temperature. The reduction of this salt in a current of hydrogen leaves a residue of osmium and silver; we can thus estimate the total osmium-silver. I have, further, estimated the silver in the form of chloride of silver by precipitating it with chloride of potassium. I obtained the following results:—

	Found.		Calculated.	
	I.	II.	Fritzsche and Struve.	Joly.
Os+Ag ..	82·8	—	84·6	82·7
Ag	—	29·8	30·6	29·9

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All these analyses confirm in a very satisfactory manner the predictions of M. Joly, and the composition of osmiamic acid should therefore be represented by the formula $OsNO_3H$. If, further, we compare the action of ammonia on osmiate of potash (which gives the osmiamate) with that of ammonia on ruthenate of potassium, which gives, as I have already shown (*Comptes Rendus*, vol. cxxii., p. 730), a nitroso-compound of ruthenium, we again find a fact supporting the hypothesis that the osmiamates are nitroso-compounds of osmium.—*Bull. Soc. Chim.*, Series 3, vol. xxi., No. 5.

ON THE COMPLEX SALTS OF PALLADIUM: PALLADOXALATES.

By M. VÈZES.

I HAVE already shown (*Bull. Soc. Chim.*, xix., 875) how the plato-oxalate of potassium, $Pt(CO_2.CO_2)_2K_2+2H_2O$, can be obtained by a simple exchange reaction starting from the corresponding chlorinised salt, the chloroplatinite of potassium, $PtCl_4K_2$. The analogy between platinum and palladium, in as far as concerns the properties of their complex salts, and particularly between the plato-salts, PtX_4K_2, and the pallado-salts, PdX_4K_2, naturally leads us to ask if the same reaction would not enable us to obtain a pallado-salt analogous to the plato-oxalate of potassium.

The existence of the salt is reasonable; Kane (*Phil. Trans.*, cxxxii., 297) in fact announced a "double oxalate of palladium and ammonium" corresponding to the formula $C_2O_4Pd.C_2O_4Am_2+2H_2O$, which he obtained by dissolving freshly precipitated palladous oxide in a solution of binoxalate of ammonia. On the other hand, Fischer (*Pogg. Ann.*, lxxi., 443), by adding, drop by drop, a solution of oxalate of potassium to a solution of palladous chloride, obtained a yellow powder, insoluble in water, which he did not, however, analyse.

I. To a warm concentrated solution of chloropalladite of potassium, $PdCl_4K_2$, we add a concentrated solution of neutral oxalate of potassium, in the proportion of 2 molecules of oxalate for 1 molecule of chloropalladite, The deep coloured solution of this latter salt is partially decoloured, and takes a yellow-brown tint; on cooling it deposits fine dark yellow needles, to which analysis (see later) gives the formula $Pd(CO_2.CO_2)_2K_2+3H_2O$, *i.e.*, a pallado-oxalate of potassium. This salt is thus formed from the chloropalladite by the exchange reaction—

$$PdCl_4K_2+2CO_2K.CO_2K=Pd(CO_2.CO_2)_2K_2+4KCl,$$

similar to the analogous method of preparing the plato-oxalate of potassium.

The same salt can be obtained by another reaction, starting with another pallado-salt—the palladonitrite of potassium, $Pd(NO_2)_4K_2$.

The transformation into pallado-oxalate cannot be effected in neutral solution, but it is possible in acid solution. If, for example, we act on a solution of palladonitrite with an excess of oxalic acid, and bring the mixture to boiling-point, the whole of the nitrogen contained in the salt will be set free in the state of nitrous fumes, and the substitution of the oxalic acid for the nitrous acid effected according to the equation—

$$Pd(NO_2)_4K_2+2CO_2H.CO_2H=Pd)CO_2.CO_2)_2K_2+4NO_2H,$$

will give pallado-oxalate of potassium, which crystallises out on cooling.

The salt thus prepared is identical with that obtained in neutral solution by means of the chloropalladite. Now the two reactions we have just mentioned, applied to the chloroplatinite and the platonitrite, give, on the contrary, two different products, the two isomerous plato-oxalates described by Söderbaum (*Bull. Soc. Chim.*, xix., 876); the pale plato-oxalate is formed in neutral solution, and the dark plato-oxalate in acid solution. We may therefore easily conclude, from this fact, that the complication brought into the study of the plato-oxalates by the existence of two isomeric varieties will not be found in that of the pallado-oxalates.

II. The analysis of the pallado-oxalate of potassium prepared by these two methods, and dried in the cold by pressure between filter-papers, has given the following results:—

1. 0·6193 grm. of material, heated to redness with an excess of sulphuric acid, gave a residue weighing 0·4168 grm.; this residue, after washing in cold water, calcination, reduction by hydrogen, and cooling in carbonic acid gas, gave 0·1593 grm. of palladium; the difference, 0·2575 grm., consisted of sulphate of potassium containing 0·1157 grm. of potassium.

2. 0·6874 grm. of material, heated to 80°, lost 0·0923 grm. of water; the residue, calcined as above with an excess of sulphuric acid, gave 0·1781 grm. of palladium and 0·2842 grm. of sulphate of potassium, containing 0·1277 grm. of potassium.

3. 0·9237 grm. of material, heated to redness with an excess of tungstic acid, gave (after passing the liberated gases over copper and oxide of copper heated to dull redness) 204 2 c.c. of carbonic acid gas at 0° and 760 m.m., weighing 0·4013 grm., and containing 0·1094 grm. of carbon.

4. 0·4725 grm. of material also gave 103·0 c.c. of carbonic acid gas at 0° and 760 m.m., weighing 0·2024 grm., and containing 0·0552 grm. of carbon.

	Calculated.		Found.			
			I.	II.	III.	IV.
Pd	105·7	25·53	25·72	25·91	—	—
2K	78·3	18·91	18·68	18·57	—	—
4C	48·0	11·60	—	—	11·85	11·68
8O	128·0	30·92	—	—	—	—
$3H_2O$	54·0	13·04	—	13·43	—	—
$Pd(CO_2.CO_2)_2K_2.3H_2O$—	414·0	100·00	—	—	—	—
$Pd+SO_4K_2$	280·0	67·63	67·30	67·25	—	—
$4CO_2$	176·0	42·52	—	—	43·45	42 84

III. The pallado-oxalate of potassium is easily soluble in warm water, but only slightly so in cold water. It is not very stable under the influence of heat. When the dry salt is kept for a long time at about 80° it loses not only its water of crystallisation, but also a certain quantity of carbonic acid gas and carbonic oxide; at the same time it becomes black, and gives, besides oxalate of potassium, which can be removed by washing, more or less oxidised palladium. Boiling its solutions causes, after a time, an analogous decomposition, which is shown by a slight metallic deposit on the sides of the glass vessel.

Simple reactions enable us to reform the two salts from which the pallado-oxalate has been prepared, viz., the chloropalladite and the palladonitrite: to effect this it suffices to produce the inverse conditions to those which have been described above.

The transformation of the chloropalladite into pallado-oxalate is effected in neutral solution; the return of the pallado-oxalate to chloropalladite takes place in acid solution. It suffices, in fact, to treat the solution with an excess of hydrochloric acid, to see the colour become much deeper; after concentration and cooling, it will give crystals of chloropalladite, mixed with colourless crystals of oxalic acid,—

$$Pd(CO_2.CO_2)_2K_2+4HCl=PdCl_4K_4+2CO_2H.CO_2H.$$

In the same manner the transformation of the pallado-nitrite into pallado-oxalate takes place in acid solution; the return of the pallado-oxalate into palladonitrite takes place in neutral solution, by the action of an excess of nitrite of potassium,—

$$Pd(CO_2.CO_2)_2K_2+4NO_2K=Pd(NO_2)_4K_2+2CO_2K.CO_2K.$$

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These reactions give evidence of the very close relations between these three salts, and thus justify the inclusion of the pallado-oxalate of potassium in the general class of pallado-salts, PdX_4M_2, which comprise nearly all the known saline compounds of palladium. There is, further, some reason for believing that, like most of the potassic pallado-salts, this pallado-oxalate may be the starting-point of a new class of pallado-salts. In fact, M. H. Loiseleur, Professor at the Libourne College, who is at present studying this subject, has already obtained, by double decomposition with nitrate of silver, a well-crystallised pallado-oxalate of silver, and he derived from this salt, by the careful action of hydrochloric acid, a pallado-oxalic acid fairly stable in moderately concentrated aqueous solution, and apparently able to furnish a complete series of metallic salts. The existence of this acid thus furnishes the proof of the complex nature of pallado-oxalate of potassium, and justifies the unitary formulæ which have here been attributed to it.—*Bull. Soc. Chim.*, Series 3, vol. xvi., No. 5.

THE CONSTITUTION OF THE AMMONIUM-MAGNESIUM PHOSPHATE OF ANALYSIS.*

By F. A. GOOCH and MARTHA AUSTIN.

(Concluded from p. 246).

Precipitation by Excess of the Magnesium Salt.

THE relations which obtain in the reverse process of precipitation—the action of the excess of the magnesium salt upon a soluble phosphate—were studied in experiments to be described. A solution of pure hydrogen disodium phosphate was prepared by carefully re-crystallising the pure salt of commerce five times from distilled water in a platinum dish, dissolving the crystals, and diluting to definite volume. The standard of the solution was established by evaporating to dryness in a weighed platinum crucible known volumes of the solution, igniting the residue, and weighing the sodium pyrophosphate. Magnesia mixture, the precipitant, was prepared by dissolving 55 grms. of magnesium chloride in as little water as possible and filtering, mixing with this solution 28 grms. of ammonium chloride purified by treating it in strong solution with bromine water and a slight excess of ammonia, filtering, diluting to 1 litre, and, after standing for some hours, filtering again.

The tests of the following table show that the precipitation of a soluble phosphate by the magnesia mixture is practically complete in faintly ammoniacal solutions even when very dilute and charged with large amounts of ammonium chloride, provided the magnesia mixture is present in sufficiently large excess.

TABLE V.

P_2O_5 in HNa_2PO_4 taken. Grm.	Magnesia mixture. C.m.³.	Volume. C.m.³.	NH_4Cl. Grms.	Precipitation.
0·0005	10	100	—	Visible at once throughout the liquid.
0·0005	50	100	—	
0·0005	10	100	10	
0·0005	10	200	60	
0·0001	50	250	60	
0·0001	10	100	—	
0·0001	10	100	10	
0·0001	50	200	10	
0·0001	10	250	60	
0·0001	50	300	60	Visible after settling out.
0·0001	50	500	60	

This conclusion was further substantiated by an actual test (by the molybdate method) of the ignited residue, obtained by evaporating a filtrate from ammonium-magnesium phosphate (equivalent to 0·8614 grm. of the pyrophosphate) precipitated by a faintly ammoniacal solution of magnesia mixture in presence of 60 grms. of ammonium chloride, which gave a precipitate of ammonium phosphomolybdate yielding 0·0002 grm. of magnesium pyrophosphate. It is evident, therefore, that any considerable deficiences of weight of the magnesium phosphate obtained by precipitating equal amounts of a soluble phosphate by magnesia mixture in presence of varying amounts of ammonium chloride, cannot be attributed to varying solubility of the magnesium phosphate under changing proportions of the ammonium chloride.

The results recorded in Section A of Table VI. were obtained by treating definite volumes of the pure solution of hydrogen disodium phosphate with magnesia mixture, in slight excess above the amount required to bring down the phosphate, and making the solution distinctly ammoniacal. After thorough subsidence, the precipitate was filtered off on asbestos under pressure in a perforated platinum crucible, washed in water faintly ammoniacal, dried, ignited, and weighed. In Experiments 1, 5, and 6, only the ammonium chloride present in the magnesia mixture was used; in the other cases weighed portions were added. In the experiments of Section B, the precipitate was dissolved in hydrochloric acid after filtering off the supernatant liquid, brought down again in dilute solution by ammonia in distinct excess, and thereafter treated as in the experiments of Section A. The experiments of Section C were conducted similarly to 1, 5, and 6 of A, excepting that the magnesia mixture was introduced into the ammoniacal solution of the phosphate drop by drop from a burette. The precipitations in A, B, and C were proved to be practically complete; for by treatment of the filtrates with more magnesia mixture and standing, no more than a trace—0·0001 grm. at the most—of the phosphate was found. The ignited residues never contained more than a mere trace of chlorine.

While the results are not entirely regular, the tendency of the ammonium salt to produce errors of deficiency in proportion to its amount is plain if we compare among themselves the experiments of A upon similar amounts of phosphate, and then those of B upon similar amounts of phosphate among themselves; and by a comparison of corresponding results in A and B it is clearly shown that the presence of an excess of magnesia mixture tends to counteract more or less completely, errors of deficiency due to the action of the ammonium chloride. These facts are quite in harmony with the hypothesis that the ammonium salt tends to produce an ammonium-magnesium phosphate richer in ammonia and phosphoric acid and poorer in magnesia than the normal salt, NH_4MgPO_4; for, though the production of such a salt in presence of an excess of the soluble phosphate compels the combination of a definite amount of magnesium with more than the normal amounts of phosphoric acid and ammonia (as was the case in the former series of experiments), when the supply of the soluble phosphate is limited the amount of magnesium associated with it must fall below the normal (as is the case in the present series of experiments). Moreover, the behaviour of the precipitant is quite in accord with the hypothesis; for, though the influence of an excess of the soluble phosphate would naturally tend (as was observed) in the same direction as that of the ammonium salt and free ammonia, viz., to the production of the phosphate deficient in magnesium, the tendency of an excess of the magnesium salt must obviously be to increase the amount of magnesium in the phosphate, as was observed in the experiments of Table VI. The hypothesis fits the facts, therefore, on both sides; and, if precipitation is practically complete (as was shown to be the case throughout) the argument for the existence of an ammonium-magnesium phosphate — poorer than the normal salt in magnesium — possibly the salt $(NH_4)_4Mg(PO_4)_2$—seems to be strong.

* Contributions from the Kent Chemical Laboratory of Yale University. From the *American Journal of Science*, Series 4, vol. vii., No. 39, March, 1899.

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TABLE VI.

	$Mg_2P_2O_7$ corresponding to HNa_2PO_4 taken.	$Mg_2P_2O_7$ found.	Error in terms of $Mg_2P_2O_7$.	Error in terms of P.	Volume.	NH_4Cl in magnesia mixture.	NH_4Cl added.	$MgCl_2.6H_2O$ in magnesia mixture.
	Grm.	Grm.	Grm.	Grm.	C.m.s.	Grms.	Grms.	Grms.
				A.				
1.	0·8615	0·8613	−0·0002	−0·00005	150	1·68	—	3·3
2.	0·8615	0·8615	0·0000	0·00000	200	1·68	20	3·3
3.	0·8615	0·8602	−0·0013	−0·00036	200	1·68	20	3·3
4.	0·8615	0·8561	−0·0054	−0·00151	300	1·68	60	3·3
5.	0·0852	0·0862	+0·0010	+0·00028	100	0·28	—	0·55
6.	0·0852	0·0866	+0·0014	+0·00039	100	0·28	—	0·55
7.	0·0852	0·0847	−0·0005	−0·00014	200	0·28	20	0·55
8.	0·0852	0·0830	−0·0022	−0·00062	200	0·28	20	0·55
9.	0·0852	0·0811	−0·0041	−0·00115	300	0·28	60	0·55
				B.				
10.	0·8111	0·8114	+0·0003	+0·00008	150,100	1·68	—,—	3·3
11.	0·8615	0·8613	−0·0002	−0·00006	150,100	1·68	—,—	3·3
12.	0·8615	0·8578	−0·0037	−0·00103	200,100	1·68	—,20	3·3
13.	0·8615	0·8487	−0·0128	−0·00358	200,100	1·68	—,60	3·3
14.	0·0852	0·0857	+0·0003	+0·00008	100,100	0·28	—,—	0·55
15.	0·0852	0·0656	+0·0004	+0·00011	100,100	0·28	10,—	0·55
16.	0·0852	0·0853	+0·0001	+0·00003	150,100	0·28	10,10	0·55
17.	0·0852	0·0819	−0·0033	−0·00092	200,100	0·28	20,20	
				C.				
18.	0·8111	0·8071	−0·0040	−0·00112	120	1·4	—	2·75
19.	0·8111	0·8052	−0·0059	−0·00165	120	1·4	—	2·75

The Practical Determination of Magnesium and Phosphoric Acid.

In determining magnesium by the procedure in ordinary use, the tendency is strong—as is shown in Experiments 1 and 2 of Table IV.—toward high plus errors, and the error is due to the combined effects of excesses of the precipitant, the ammonium salt, and free ammonia. The Experiments 11 and 12 of B, Table III., show conclusively that such tendencies to error may be counteracted effectively by pouring off the supernatant liquid (through the filter to be used subsequently to collect the precipitate) as soon as the precipitate subsides, dissolving the phosphate in the least amount of hydrochloric acid, bringing it down again, after dilution, by a faint excess of ammonia, filtering (best, we think, on asbestos under pressure), washing with faintly ammoniacal water, and igniting as usual.

Many years ago (*Am. Journ. Sci.*, [3], v., 114) a method of precipitating the ammonium-magnesium phosphate was advocated by Professor Wolcott Gibbs, which consists essentially in boiling the solution of the magnesium salt with microcosmic salt and adding ammonia after cooling, and by which most exact analytical results were obtained. Our experience confirms completely that of Dr. Gibbs, and we desire to direct attention again to a procedure the advantage of which has, unfortunately, not been broadly known and accepted. Even in the presence of considerable amounts of ammonium chloride this process yields a phosphate of nearly ideal constitution if only the boiling be prolonged from three to five minutes. The greater part of the ammonium-magnesium phosphate—about 90 per cent—forms in this process before free ammonia is added, and the ammonium which enters the phosphate thus formed is derived from the microcosmic salt, which must become correspondingly acidic. Under these conditions, the tendency to form an insoluble ammonium-magnesium phosphate richer in ammonia and poorer in magnesia than the normal salt, does not develop. In the process of Dr. Gibbs, as well in the modified precipitation process in the cold, the use of the faintly ammoniacal solution and wash-water is sufficient and advantageous.

In the precipitation of a soluble phosphate by magnesia mixture, the tendency of the precipitant and that of the ammonium salt are antagonistic, so that the effect of the latter salt is somewhat masked, though manifest. This opposition of effects has been noted by Mahon (*Journ. Am. Chem. Soc.*, xx., 445), who, though regarding the actual attainment of an exact balance as uncertain, ventures the opinion that accurate results should be attainable by the careful relative adjustment of the proportions of the precipitant and ammonium salt. Mahon claims to get the best results by a very gradual addition of magnesia mixture to the ammoniacal solution of the phosphate containing about 16 per cent of ammonium chloride, strong ammonia being added subsequently. From our observations, however, recorded in Section C of Table VI., it appears that the method of introducing the magnesia mixture gradually into the ammoniacal phosphate (taken in quantity sufficiently large to give unmistakable indications) produces a precipitate deficient in magnesium, and so leads to errors of deficiency in the phosphorus indicated. The use of strong ammonia, moreover, we have shown to be both unnecessary and disadvantageous. Our experiments go to show that good results may be expected when the solution of the phosphate containing a moderate excess of the magnesium salt and not more than 5 to 10 per cent of ammonium chloride is precipitated by making it slightly ammoniacal—the precipitate being washed in slightly ammoniacal wash-water. In general, however, and especially when more ammonium chloride than this proportion, or more magnesium salt than twice the amount theoretically necessary, is present, it is safer to decant the supernatant liquid from the precipitate (through the filter to be used subsequently to hold the phosphate), to dissolve the precipitate in a little hydrochloric acid and re-precipitate by dilute ammonia, washing with faintly ammoniacal wash-water.

Relative Speeds of Saponification of the Ethers of the Higher Homologues of Oxalic Acid.—E. Hjelt.—The author has found that the speed of saponification diminishes regularly as the carboxyls are further one from the other; while, on the contrary, the degree of dissociation of the second atom of hydrogen gradually increases.—*Berichte der Deutsch. Chem. Gesell.*

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PRESIDENTIAL ADDRESS TO THE IRON AND STEEL INSTITUTE.

By Professor Sir W. ROBERTS-AUSTEN, K.C.B., D.C.L., F.R.S.

(Continued from p. 249).

1846. It is perhaps natural that in the rest of the first half of the century the most noteworthy feature seems to be the renewed attention devoted to the investigation of the nature of oxidation and reduction. As the investigations, which were of great importance, were mainly conducted on the Continent, I must reluctantly leave their consideration until a future meeting. In the blast-furnace there was evidently a kind of tidal ebb and flow in the relations of carbon and of oxygen, resulting sometimes in reduction, and at others in oxidation or carburisation; but the changes were all capable of more or less simple expression if viewed either from the atomic or the dynamic standpoint. As the furnaces grew in dimensions, their flaming tops threw a lurid glare over the country, and, "like the dying sunset kindled through a cleft," revealed the magnitude of the problems involved in blast-furnace practice, which were seen to be disproportionate to their apparent simplicity.

As regards the study of the nature of the ascending gaseous column, I may anticipate the remarks I shall have to make next year by pointing out that the labours of the illustrious chemist Bunsen were shared by the late Lord Playfair, and that a joint communication of theirs was published in the Report of the British Association for the year 1846.

In the first half of the century efforts were directed mainly to obtaining a material,—cast-iron containing some 3½ per cent of carbon, and fusible at a temperature readily attained in the blast-furnace. In the second half of the century, while efforts to obtain this fusible material were increased, attention was also directed to removing the carbon, and obtaining a product which had a melting-point of 400° C. (720° F.) higher than cast-iron. This product was either cast directly into ingot moulds or recarburised to the extent necessary to constitute the various gradations of steel. Sheffield hardly knew steel except as a material to be used for the manufacture of cutlery, for which she had been famous since the time of Chaucer.

It is characteristic of our British methods that special circumstances and needs, mainly arising in connection with the development of the steam-engine and railways, revealed the broad principles by which the production of iron must be governed. It was natural, therefore, as time went on, that in the work of successive inventors the guidance of scientific principles became progressively evident as ill-directed efforts were gradually replaced by the results of systematic experiments.

1850-51. The second half of the century began with events of strange importance. The Great Exhibition revealed our industrial strength to all nations. The official reporter of the Metallurgical group states that 2,250,000 tons of pig-iron were annually produced in this country, and that its estimated value was £5,400,000. The annual production had risen in fifty years from 200,000 tons to over two and a quarter millions. Sheffield produced at the opening of the century 35,000 tons of steel, of which 18,000 tons were cast-steel. Messrs. Turton exhibited a single ingot of steel weighing 2688 lbs., but Krupp showed an ingot of double the weight, for our country was only preparing for the great change which was so soon to enable it to lead the steel manufacture of the world.

A noteworthy feature of the Exhibition was the collection of iron ores of this country exhibited by Mr. Blackwell, who subsequently, and most generously, provided a large sum towards the cost of their analysis. With reference to this collection, the reporter points out that in this country "the ores are not carried far, except where there is great facility for transport." This is noteworthy, as before the century was much older an important supply of ore was brought from Spain, and in the near future we may even seek a supply for British furnaces from distant parts of our own Empire.

The year 1851 was, moreover, an important one for metallurgy in this country, as it saw, by the wisdom of H.R.H. the Prince Consort, the establishment of the Institution which developed into the Royal School of Mines. If the projected scheme of instruction had been fully carried out, the establishment of a general system of technical instruction, which the pressure of necessity is slowly forcing upon us, would have been anticipated by forty years.

In the year of the Great Exhibition the blast-furnaces seldom exceeded 50 feet in height, and it was not until 1864 that Mr. John Vaughan erected a furnace 75 feet high, with remarkable results as regards increased output; since then the gigantic furnaces of the Cleveland district have become common.

1856. The year 1856 will be ever memorable in the metallurgical annals of our nation as that in which Bessemer gave the description of his process to the world at the Cheltenham Meeting of the British Association. As regards the process itself, we have too lately lost our great countryman, and many of us are too familiar with the details of his labours to be able either to fully estimate its value or to realise the wonder of its results. Let us try to think of the Bessemer process as I believe those at the end of the twentieth century will, whose views range over a wider perspective than we can command. The economic aspect of the question will naturally strike the metallurgists of the twentieth century. They will see that in 1855 the make of steel in Great Britain did not exceed 50,000 tons, and the cost of the steel produced sometimes reached £75 a ton. They will see that thirty years after the publication of Bessemer's paper the production of Bessemer steel rose to 1,570,000 tons, and that ship plates were sold at £6 10s. a ton. It will be noted that before the century closed, the maximum production of Bessemer steel in this country in one year reached 2,140,000 tons. The scientific aspect of the process will, however, excite their widespread interest, for before the end of the twentieth century metallurgy will be taught in our older universities. It will be seen that, notwithstanding the title of Bessemer's Cheltenham paper, he recognised and insisted on the fact that the intense heat was engendered by the combustion of the elements within the fluid bath. It will be noted in what close relation the purely scientific work of Thomas Andrews of Belfast, on the heat of combination, stands to that of Bessemer, and that another instance is presented of the dependence of industrial work on pure investigation. Bessemer's proposal to employ a mixture of steam and air will not be ridiculed as it has been, for speculation will be rife as to whether he did not hope that the liberated hydrogen might remove sulphur and phosphorus, notwithstanding the feebly exothermic result of the ensuing combination, and in spite of the cooling effect of water-vapour. In view of the fact that endothermic combinations take place at a high temperature, the possible action of hydrogen as a decarburiser will be dwelt upon. Prof. Noel Hartley's papers upon the Thermo-chemistry of the Bessemer Process will be read with much interest. Surprise will, however, be widely felt that physicists generally of the last half of the nineteenth century did not see in the lovely flames of lilac, amethyst, gold, and russet, or in the "stars suspended in a flying sphere of turbulent light" which come from the converter, an appeal to fully investigate their cause and to study the dynamic problems presented by the intense heat engendered. Why was not the destination ascertained of the 1000 cubic feet of argon which accompanies the air passing through the metal during an ordinary Bessemer 10-ton blow? Why were not more strenuous efforts made to ascertain the

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effect of the temperature of the bath on the nature of the metal?

It will be felt that, as the eighteenth century had closed with a clear statement as to the true nature of oxidation, the nineteenth century had seen its magnificent application in the Bessemer process.

As regards the work of Mushet, future generations will, I believe, desire to add nothing to the words of the President of this Institution, who, in 1875, had the pleasure of awarding the Bessemer Medal to him. Mr. Menelaus then said "that the application of spiegeleisen . . . was one of the most elegant, as it certainly was one of the most useful, inventions ever made in the whole history of metallurgy."

1861. Attention must now be directed to the great process for the production of steel which involved the use of the "open hearth."

Sir William Siemens's life was one long and ultimately brilliantly successful effort to apply the kinetic theory of gases and the dynamical theory of heat to industrial practice. He was eminently a practical worker; but the depth and accuracy of his scientific knowledge gives him a place near that of all the great atomists from the time of Lucretius to that of our own countrymen, Graham, Joule, Clerk Maxwell, and Kelvin. In many of Siemens's papers, theory and practice are closely blended. In viewing the results of his labours, it will be seen in future ages that confidence in the trustworthy character of steel was finally established by experiments on metal produced in the regenerative furnace of Siemens. Looking back, it is astonishing with what difficulties the use of steel for structural purposes was beset. In 1859 Sir John Hawkshaw was not permitted by the regulations of the Board of Trade to employ steel in the construction of the Charing Cross bridge. Time will not permit me to indicate the efforts which were made to induce the Board of Trade to remove the serious hindrances to the use of steel, which had "rendered the construction of the projected bridge over the Firth of Forth practically impossible." These efforts were not successful until 1877, when a Committee, consisting of Sir John Hawkshaw, Colonel Yolland, and Mr. W. H. Barlow, were able to recommend that the employment of steel in engineering structures should be authorised by the Board of Trade. The steel employed was to be "cast steel, or steel made by some process of fusion, subsequently rolled or hammered"; one condition of such recommendation being that "the greatest load which can be brought upon the bridge or structure, added to the weight of the superstructure, should not produce a greater strain in any part than 6½ tons per square inch."

As regards the use of steel for shipbuilding purposes, in this same year, 1875, Sir Nathaniel Barnaby asked, "What are our prospects of obtaining a material which we can use without such delicate manipulation and so much fear and trembling?" He partly answered his own question, four years later, when he quoted experimental evidence as to "the recent successes" of open-hearth steel. In 1890 he completed the case by pointing out that naval architects now "have a perfectly regular material, stronger and more ductile than iron," and he speaks of "our lasting debt of gratitude for the birth and training of that true prince, William Siemens." It is hardly necessary to point out that the country owes the excellent materials used in naval architecture mainly to the productions of the regenerative furnace.

In connection with the production of mild steel, the addition of ferro-manganese to the decarburised bath proved to be most effective. We can hardly over-estimate our indebtedness to those whose perseverance ensured the adoption of mild steel for maritime and other purposes. "Looked at from the standpoint of to-day, when thousands of tons of such steel are made weekly without serious anxiety or trouble, it is scarcely possible to realise the anxieties and difficulties of the days when the manufacture of open-hearth steel was being perfected." To no one is our debt greater than to our Vice-President, Mr. James Riley, who bore a large share of the anxieties of the early days, and whose words are those I have just quoted.

With regard to the great modifications which have been effected in the Bessemer and open-hearth processes, reference must be made to that ample source of information, our *Journal*. It must also be consulted for the history of the appliances for heating the blast with which the names of Cowper and of Whitwell will always be specially connected.

In speaking of Bessemer and Siemens I have been obliged to depart somewhat from strict chronological order. I must now resume it at the year 1865.

1865. Sir Joseph Whitworth patented on November 24, 1865, a process for submitting liquid steel to heavy pressure, at the critical juncture when the metal is passing from the fluid to the semi-fluid state, to prevent any part of the casting from becoming hollow or unsound.

1866. In the year 1866 Graham's first paper on the occlusion of gases by metals was published in the *Philosophical Transactions*. Its results have been far-reaching, and will always be regarded as one of the metallurgical triumphs of the century.

1869. In the year 1869 our Institute was founded. In view of certain aspects of the treatment which inventors had previously received from their industrial brethren and from the country, it will be evident that the time for its formation had fully come. Taking instances almost at random, I may remind you that Dud Dudley was, as he says, "with lawsuits and riots wearied and disabled" in the seventeenth century, and that Henry Cort was neglected and oppressed in the eighteenth. The great invention of iron bottoms in the puddling-furnace made by Rogers was received with ridicule, and he died in poverty. Popular tradition of Sheffield indicates that possession was obtained of Huntsman's secret "by the heartless trick of a rival." Neilson, though he warmly acknowledges the support he received from certain iron-masters, was treated with singular meanness by others. Heath fought single-handed for fifteen years "against a common purse, the accumulation of the wealth which he had created." Even Bessemer's early statements were received with incredulity and contempt. With the formation of our Institute all this is changed: men place the results of their work and experience freely at the disposal of their brethren, and each fresh advance meets with appreciative consideration. "Vigorous moderateness," wrote the late Walter Bagehot, "is the rule of a polity which works by discussion. . . . It was government by discussion that broke the bond of ages and set free the originality of mankind."

1869-71. The history of our industry since the formation of this Institute is epitomised by the labours of those who have hitherto occupied the Presidential chair. The Duke of Devonshire, K.G., our first President, worthily sustained the honour of the name of Cavendish, one of the most illustrious in the scientific annals of our country, and the connection of the Duke with the iron industry of Barrow is an incident of the first importance in our industrial records. He highly appreciated the importance of science in relation to the progress of the nation; and the Report of the Royal Commission on Scientific Instruction and the Advancement of Science, of which he was President, contributed in no small degree to the awakening of public attention to the subject. His noble foundation of the Cavendish Laboratory at the University of Cambridge stimulated research on lines closely connected with this Institute, as the work of Clerk Maxwell, of Rayleigh, of J. J. Thomson, of Ewing, and of Heycock and Neville, abundantly testify. It is certain that the main efforts of his life were directed to developing the resources and improving the condition of the people. Neither rank, wealth, nor intellectual gifts had power to affect the simplicity of his character or to lessen the deep sense of duty which controlled all his actions.

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1871-73. The life-work of our second President, Sir Henry Bessemer, has already been dealt with, and the lesson it teaches is how vastly important the labours of one man may be to a nation. In these days the facilities for work are much greater than they were, and results are obtained by an army of workers; but, as Stanley Jevons has pointed out, the influence of the individual genius is "not withering, but is growing with the extent of the material resources which are at his command." It was during the Presidency of Sir H. Bessemer that Snelus patented the use of basic lining for furnaces and crucibles, which was ultimately found to be so important in relation to the elimination of phosphorus from pig-iron.

1873-75. Sir Lowthian Bell embodies for us the progress in blast-furnace practice of at least the last half-century. It was under his Presidency that the first Continental meeting was held, the place chosen being Liége, Belgium's great metallurgical centre. He was the author of the first paper communicated to the Institute, choosing as a subject "The Development of Heat and its Appropriation in the Blast-Furnace." There is a passage in the Presidential Address of Dr. Percy, with reference to the work of Sir Lowthian Bell, which I may be permitted to quote. Dr. Percy said:—"His laborious, careful, and original investigations of scientific problems of the highest interest in the metallurgy of iron and steel, must be so well known to this audience that any comment upon them from me would be superfluous, if not presumptuous." If Dr. Percy, the metallurgical historian of the age, thus shrank in 1885 from the attempt to give adequate expression to the value of Sir Lowthian's work, it would be impertinent in me to say more than that the fourteen years which have passed since Dr. Percy wrote have only served to bring into greater prominence Sir Lowthian's unswerving devotion to the solution of those problems he has so patiently studied.

1875-77. Attempts to improve the ancient operation of puddling by the aid of mechanical appliances, received their fullest development under the guidance of William Menelaus. The great usefulness of his career may perhaps be well indicated by the statement that he was among the first to be convinced of the vast superiority of steel to puddled iron, and urged its adoption with singular foresight and vigour. His position as manager of Dowlais Works gave great force to his advocacy. By lending his great mechanical resources and power of organisation to scientific research, he brought about some of the greatest improvements that were ever effected in the iron and steel industries. He associated himself, moreover, with Edward Riley, who, as an analytical chemist, subsequently made a distinguished name.

1877-79. The work of Sir William Siemens has already been dealt with as fully as time will permit. I will, therefore, only quote the public tribute to his memory which was offered at the time of his death in 1883:—"The nation at large has lost a faithful servant, chief among those who live only to better the life of their fellow-men by subduing the forces of Nature to their use. Looking back along the line of England's scientific worthies, there are few who have served the people better than this, her adopted son—few, if any, whose life's record will show so long a list of useful labours."

1879-81. Edward Williams shares with Menelaus the unique distinction of having been the first to appreciate the great importance of Bessemer's discovery, and within three days after the publication of Bessemer's paper at the British Association he erected at the Dowlais Works a small fixed converter, had blown pig-iron, and had rolled the product into bars, "to the great astonishment of all concerned." His vigorous address as President of this Institute was remarkable for the then prophetic expression of belief, that the day was "at hand when either by a Bessemer converter or by the open-hearth . . . there will be produced with absolute certainty, with comparatively light labour, and (he hoped) with fair profit to all concerned, every kind, variation, and quality of the metal iron which we rudely designate steel and wrought iron." He also made a striking appeal to educated intellectual young men who "hung listlessly" about the professions "to break through the absurd old prejudice against seemingly rough work, and come over to the healthy business of iron and steel-making, in which they might render the world good service."

1881-83. Josiah Timmis Smith, in his Presidential Address, gave a remarkable retrospect of the period which had elapsed since the foundation of the Institute. He showed that, comparing the year 1880 with the year 1869, 2¼ millions more tons of iron had been made with the same amount of fuel, or we had, in fact, economised our fuel supplies to the extent of 10,000,000 tons. He gives a masterly summary of the progress in our industries, and eloquently pleaded that chemistry had proved its claims to be regarded as the handmaid of the iron manufacturer, and had given our metallurgical art a place in relation to the exact sciences which it could never otherwise have occupied. He also urged with great force that our Institute had broken down the spirit of exclusiveness and prejudice, that is usually the most rampant where knowledge is most wanting.

1883-85. To Sir Bernhard Samuelson is due the credit of being the first to succeed in convincing the House of Commons of the national importance of Technical Education in its widest sense, and to induce it to grant a Select Committee to inquire into the provisions for giving instruction in theoretical and applied science to the industrial classes. I wish I knew which of his wise and careful utterances he would like me to quote. Left to my own choice, I reject reference to his elaborate array of statistics, and select the following brief passage from his Presidential Address:—"It is to the further development of the world's railways that we must mainly look in the future as in the past for the support of our trade." Bearing in mind what is happening in Egypt, in South Africa, in China, and on the frontiers of our Indian Empire, the vast importance of railways, to which Sir Bernhard refers, cannot be doubted. Hence the engineer, considered as a pioneer, is absolutely dependent for steel rails and for the material for the construction of bridges on the metallurgist, whose work is the real foundation of progress. One other sentence, which is typical of the whole tenor of his life's work, may be quoted:—"It is in the mutual co-operation (in a scientific spirit) of every grade in our great craft that we may build up the hope, nay, that we may cherish the certain expectation, of placing it on even a higher eminence than that which it has already attained.

(To be continued).

Royal Institution. — Forthcoming Centenary Celebrations.—In the month of June the Royal Institution of Great Britain will complete one hundred years of its existence, the first meeting of its Members in the building in Albemarle Street having been held on the 5th June, 1799. The Managers have decided that this event, so interesting and memorable in the life of the Institution, and in the history of science in this country, should be duly celebrated. They have, therefore, arranged for the delivery of two Commemoration Lectures. The first of these Lectures will be delivered at 3 o'clock on Tuesday, the 6th of June, by Professor Lord Rayleigh, when His Royal Highness the Prince of Wales, Vice-Patron of the Institution, will preside and receive the Honorary Members; the second of these Lectures will be delivered at 9 o'clock on Wednesday evening, the 7th of June, by Professor Dewar, when His Grace the Duke of Northumberland, President of the Institution, will preside. It is further announced that the Lord Mayor has, in the kindest manner, consented to give a reception to the Members, Foreign Guests, and Representative Men at the Mansion House, on the evening of Tuesday, the 6th of June.

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PROCEEDINGS OF SOCIETIES

CHEMICAL SOCIETY.

Ordinary Meeting, May 18th, 1899.

Professor Thorpe, F.R.S., President, in the Chair.

Messrs. H. H. Bowles, F. S. Young, and R. Haliburton Adie were formally admitted Fellows of the Society.

Certificates were read for the first time in favour of Messrs. George Dekeyne Atkinson, care of Crowley and Co., The Brewery, Alton, Hants; James Connah, Geralton, Carlton Road, Sidcup; Robert McClumpha, 372, Westgate Road, Newcastle-on-Tyne; Eskricke Sidney Phillips, Christ's College, Cambridge; John William Shepherd, 48, Ovington Street, S.W.; Charles Simmonds, 17, Ruvigny Gardens, Putney, S.W.

Of the following papers those marked * were read:—

*71. "*Corydaline.*" Part VI. By James J. Dobbie and Alexander Lauder.

In this paper the authors give the results of the investigation of *corydaldine*, $C_9H_7NO(OCH_3)_2$, one of the substances obtained by the oxidation of corydaline by means of potassium permanganate (*Trans.*, 1894, lxv., 57). By employing a smaller proportion of permanganate and using it at the ordinary temperature, a larger yield was obtained than by the method previously described.

Corydaldine readily dissolves in water, melts at 175°, and contains two methoxyl groups. Dissolved in hydrochloric acid and treated with sodium nitrite at 0°, a yellow nitroso-derivative is obtained (m. p. 185°), which is very insoluble in hot and cold water. When this nitroso-derivative is gently warmed with a solution of sodium hydrate, nitrogen is evolved, and on addition of hydrochloric acid to the solution a new substance, melting at 138—139°, is obtained, which is the anhydride of a monobasic acid. Its formula is $C_{11}H_{12}O_4$; it is difficultly soluble in cold but readily in boiling water, from which it crystallises well on cooling. Treatment with hydrogen iodide proves that it contains two methoxyl groups, and oxidation with permanganate at 100° converts it into metahemipinic acid. Heated with hydrochloric acid at 150°, a phenolic derivative (m. p. 232°) is obtained, which shows all the reactions of ω-hydroxyethylcatecholcarboxylic anhydride obtained by Perkin from berberine (*Trans.*, 1890, lvii., 1028). The authors therefore conclude that *corydaldine* only differs from ω-amidoethylpiperonylcarboxylic anhydride in having two methoxyl groups instead of the piperonyl group, and that it is closely related to oxy-hydrastinine.

Corydaline is thus proved to be closely related to berberine, hydrastine, narcotine, and papaverine, in common with which it contains an isoquinoline nucleus. When the alkaloid is oxidised at 100° by means of potassium permanganate, the chief product is a mixture of hemipinic and metahemipinic acids.

The substance previously described under the name of corydalineic acid (*Trans.*, 1894, lxv., 57) is found to be an acid ammonium salt of metahemipinic acid, having the formula $C_{10}H_{10}O_6.C_{10}H_9O_6(NH_4).3H_2O$.

*72. "*Oxidation of Furfural by Hydrogen Peroxide.*" By C. F. Cross, E. J. Bevan, and T. Heiberg.

The results described in this paper are obtained by interaction of the aldehyde and peroxide in dilute aqueous solution (2—4 per cent furfural) at 40° in presence of iron salts in small quantity. The peroxide is added until the characteristic reaction of the aldehyde with aniline acetate is no longer obtainable, the quantity of peroxide required being 2 to 3 molecules per molecule of furfural.

The main product of oxidation is recognised by its reactions with phenylhydrazine (formation of hydrazone), and with phloroglucinol and hydrochloric acid (deep red-violet colouration followed by precipitation of the colouring matter) to be a furfural derivative. Analysis of the hydrazone shows it to be the hydrazine derivative of a *hydroxyfurfural*. Along with this main product is an acid, which is easily separated as a barium salt insoluble in acetic acid. Analysis of the barium and lead salts show the acid to be the corresponding *hydroxypyromucic* acid.

The substitution of hydroxyl for hydrogen in the furfurane nucleus agrees with the results of previous investigations as to the mode of action of the peroxide; but, as a further confirmation, its action on benzene under conditions similar to those in the above described experiments has been so far studied as to prove the formation of a considerable quantity of phenol. The furfural-phenol corresponds to an oxybenzaldehyde; reasons are given for regarding the OH and CHO-groups as occupying the 1 : 2-positions. It is noteworthy that, as in the case of the normal saturated "carbohydrates," the CHO-group is but slowly attacked by the peroxide relatively to a CH-group.

The further action of the peroxide is destructive in character, the furfurane ring being being broken down, the chief product being formic acid, along with some acetic and oxalic acids. The intermediate products appear from their reactions to be hydroxyketonic acids. The formation of methylated compounds is probably a secondary result of the decomposition; from the products of the original reaction, iodoform is obtainable in some quantity, and the amounts have been estimated.

Special interest attaches to the hydroxyfurfural which has been thus obtained. Its reactions with phloroglucinol andwith resorcinol in presence of HCl are similar to those of the lignocelluloses. These colours may be developed on a pure cellulose cloth or paper for comparative study. It is then seen that the brilliant colours of the original products—blue with resorcinol, violet with phloroglucinol, give place to "flattened" shades, grey and brown respectively, on washing with ordinary water.

By means of these reactions, it is now shown (1) that a furfural-phenol is a constituent of the lignocelluloses; (2) that the colour reactions of these "natural" products with the hydroxybenzenes are due to the presence of such compounds; (3) that the equally characteristic reactions of the lignocelluloses with aniline salts are reactions with a second constituent group, *e.g.*, the keto-R-hexene complex.

A furfural-phenol being a normal product of the condensation processes accompanying lignification, it is probably also a product of the action of the condensing acids used in estimations of furfural. It appears, therefore, that the furfural actually isolated does not necessarily represent the entire production of furfurane derivatives; and these observations supply the basis for a further differentiation of the complex group of furfural-yielding plant constituents or furfuroids.

Discussion.

Mr. F. S. Young said that, as the result of some preliminary experiments, he had found that, although hydrogen peroxide by itself attacks benzene only very slowly, an extremely energetic reaction takes place in the presence of ferrous salts. A complete examination of the products of the reaction has still to be made; but he had proved that a considerable quantity of phenol is formed.

In two preliminary experiments, in which 1 molecule and 2 molecules of hydrogen peroxide were used for 1 molecule of benzene, the yield of phenol was 10 per cent and 20 per cent respectively; and it is possible that this yield may be increased when the most favourable conditions for its formation have been determined. Pyrocatechol was also obtained as a product of the reaction.

Mr. Fenton said that the results obtained by Messrs. Cross and Young with furfural and benzene, together with those which had been observed by himself and others in the case of phenol, appeared to establish a third typical reaction of hydrogen peroxide in presence of iron, —namely, the replacement of hydrogen by hydroxyl.

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With reference to Mr. Cross's suggested explanation of the mechanism of the reaction, he did not think that it was applicable to the cases which he (Mr. Fenton) had studied, since other oxidising agents might be substituted for the hydrogen peroxide.

Mr. Cross, in reply, said with regard to the mechanism of the action of hydrogen peroxide, that although the tendency of the peroxide to split into hydrogen and oxygen might not be suggested by the interactions with inorganic compounds, yet its behaviour with carbon compounds, especially those which are unsaturated, might furnish evidence of such intermediate phases as would disappear in the final stages of the reaction.

*73. "*Note on the Reactions between Sulphuric Acid and the Elements.*" By R. H. Adie.

The publication of a paper by M. Berthelot on the action of sulphuric acid on metals (*Ann. Chim. Phys.*, 1898, [vii.], xiv., clxxvi., 176—204), leads the author to publish the results of some experiments which he performed some years ago. The results obtained by Berthelot in the case of zinc confirm those of Muir and the author (*Trans.*, 1888, liii., 47, and, in the case of copper, those of Pickering (*Trans.*, 1878, xxxiii., 112). In the following table, the temperatures of decomposition of sulphuric acid by the easily obtainable elements are given, these being grouped according to the periodic system.

It appears possible, even at this stage, to draw a few conclusions:—

(i.) Sulphuric acid is decomposed by most elements with the formation of sulphur dioxide and hydrogen. Sulphuretted hydrogen only appears as a special impurity in a few cases.

(ii.) In any group of elements the decomposition temperature becomes lower as the atomic weight of the element increases.

(iii.) Copper, nickel, and palladium, all form black sulphides, and also all give compounds with ammonia.

(iv.) In the case of zinc, a pure specimen (kindly given by Professor Ramsay) caused the temperature of decomposition to rise to 250°. With this specimen, no hydrogen sulphide was evolved up to the boiling-point of the acid. This suggests the unsuitability of ordinary zinc for further work.

Element.	SO_2 appears.	H_2S appears.	Notes.
Hydrogen	170°	None	Gas prepared from Zn and HCl washed and dried with H_2SO_4.
Copper	Begins 110—115° Continuous 120°	None	Cu_2S formed.
Silver	175°	None	Gas evolved at 150°.
Magnesium	215°	Trace	
Zinc	250°	None	SO_2 evolved as soon as reaction starts.
Cadmium	205°	Trace?	
Mercury	120°	None	Gas given off at 110°.
Aluminium	235°	None	No bubbles of SO_2.
Carbon	188°	None	
Tin	145°	None	S formed.
Lead	140°	None	
Thallium	Below 20°	Below 20°	Formed at once at ordinary temperature. Brown solid formed.
Arsenic	110°	None	No AsH_3.
Antimony	90—95°	None	
Bismuth	90°	None	Gas evolved at once.
Sulphur	200°	None	Melts at 220°. No bubbles till 230°.
Selenium	170°	None	
Molybdenum	135°	None	Gas begins at 115°. Green solid formed.
Tungsten	175°	None	
Manganese	155°	None	Gas evolved at 120°.
Iodine	—	—	Passes over at 92°. No action before.
Iron	220°	None	Gas evolved at 170°.
Nickel	145°	None	Black solid formed.
Cobalt	240°	None	
Palladium	200°	None	Reaction not vigorous. Blackens from formation of sulphide.
Platinum	None	None	

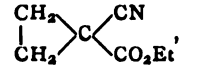
The author intends to make a fuller investigation of some of the more definite reactions.

74. "*On the Action of Ethylene Dibromide and of Trimethylene Dibromide on the Sodium Derivative of Ethylic Cyanacetate.*" By H. C. Harold Carpenter and William H. Perkin, jun.

One of the great difficulties in investigating the derivatives of trimethylene is the fact that the condensation of ethylene bromide with the sodium compounds of ethyl malonate and ethyl acetoacetate gives only a very small yield of trimethylene compounds (*Trans.*, 1885, xlvii., 808); and again, in investigating the formation of tetramethylene compounds by the action of trimethylene bromide on the sodium derivative of ethyl malonate, the best yield of ethyl tetramethylenedicarboxylate (1, 1) obtained was only 33 per cent (*Trans.*, 1887, li., 3).

It appeared to us possible that the yield of these closed-chain compounds might be considerably increased if ethyl cyanacetate was substituted for ethyl malonate and acetoacetate, and this has been found to be the case.

Ethyl trimethylenecyancarboxylate (1, 1),—



of which 50—60 per cent is obtained by the action of ethylene bromide on the sodium derivative of ethyl cyanacetate, is a colourless mobile liquid boiling at 210—211° under 766 m.m. pressure, $\Delta\ 0°/4° = 1{\cdot}0783$. It dissolves gradually in aqueous ammonia (sp. gr. = 0·88) forming the amide, which crystallises in lustrous needles (m. p. 160°). Cold methyl alcoholic potash saponifies it instantly, with the production of the potassium salt of *trimethylenecyancarboxylic acid* (1, 1). The acid is obtained in the form of long colourless prisms by the evaporation of its ethereal solution in a stream of dry air. It melts undecomposed at 148°. It is remarkable that all attempts to split off the carboxyl group and prepare cyantrimethylene, (i.) by distilling the acid, (ii.) by heating it in sealed tubes with a small quantity of water, (iii.) by heating the silver salt, have failed. Recently, however, this substance has been prepared by L. Henry, who distilled γ-chlorbutyronitrile repeatedly over solid potash and obtained it in the form

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of a colourless liquid of pleasant odour. B. p. = 135°, Δ 16° = 0·911 (*Bull. Acad. Roy. Belgique*, 1898, [3], xxxvi., 34; 1899, [3], xxxvii., 17—22).

The silver salt is a very characteristic substance. It is soluble in water, and crystallises from its aqueous solution in lustrous prisms. The conversion of the trimethylenecyancarboxylic acid into trimethylenedicarboxylic acid is best effected by boiling with aqueous potash. From the latter acid, its characteristic derivative, bromethylmalonic acid (m. p. 116°) was prepared by the action of aqueous hydrobromic acid (sp. gr. = 1·83).

The condensation of ethylene bromide with the sodium derivative of ethyl cyanacetate yields, besides the trimethylene derivative, two crystalline substances, the one melting at 119°, the other at 95—96°, according as the reaction is made to take place under pressure in soda-water bottles or at ordinary pressures. These substances have been analysed, but their constitutions have not yet been discovered.

Ethyl tetramethylenecyancarboxylate (1, 1),—

$$\begin{matrix} CH_2—CH_2 \\ | \quad\quad | \\ CH_2—C(CN).CO_2Et \end{matrix}$$

is obtained to the extent of 60—70 per cent by the action of trimethylene bromide on the sodium derivative of ethyl-cyanacetate. It is a colourless liquid boiling at 213—214° under 766 m.m. pressure, Δ 0°/4° = 1·0633. It dissolves in aqueous ammonia (sp. gr. = 0·88), but the resulting amide is easily soluble and does not crystallise out. Cold methyl alcoholic potash saponifies it at once, forming the potassium salt of *tetramethylenecyancarboxylic acid* (1, 1). The free acid is purified by crystallisation from carbon disulphide containing a small quantity of ether, and is thus obtained in long silky needles, which have the remarkably low melting-point 69—70°. By careful heating they may be sublimed unchanged. The silver salt is completely analogous to that of the corresponding trimethylene acid. Boiling aqueous potash hydrolyses the cyanogen group, and the product is tetramethylenedicarboxylic acid (1, 1), which melts at 157°. The characteristic lead salt was prepared and analysed. The by-product in the preparation of the ethyl tetramethylenecyancarboxylate is an oil. The investigation of this substance is in progress.

75. "*The Maximum Vapour-pressure of Camphor.*" By R. W. ALLEN, M.A.

By the two methods which he employed in determining the vapour-pressures of naphthalene (*Proc.*, 1899, xv., 122), the author has determined the maximum pressures of camphor vapour from 0—80°. The results obtained by these methods agree throughout, but differ very notably from those obtained by Ramsay and Young (*Phil. Trans.*, 1884, clxxv., 45).

PHYSICAL SOCIETY.

Ordinary Meeting, May 26th, 1899.

Mr. T. H. BLAKESLEY, Vice-President, in the Chair.

A PAPER by Prof. S. YOUNG and Mr. ROSE-INNES, on "*The Thermal Properties of Normal Pentane*," Part 2, was read by Mr. ROSE-INNES.

In the first paper on this subject, read before the Physical Society last December, it was shown that the relations existing between the volume temperature and pressure of normal pentane could be closely represented by the equation—

$$p = \frac{RT}{v}\left\{1 + \frac{e}{v + k - gv^{-3}}\right\} - \frac{l}{v(v + k)}.$$

This formula was first used in connection with isopentane, and it has been shown that the values of R and l/e are the same for the two isomers. The authors find that, if l and e be taken separately equal to each other, and if the constants k and g be calculated from experiments on normal pentane, errors of 2 per cent occur between the calculated and experimental results. This point has been investigated both algebraically and graphically, and the supposition that these constants are separately equal has been thought incorrect. Taking the values of R, l/e, and g as being the same in the two pentanes, the constants l and k have been determined, and by this means the relations between volume temperature and pressure have been represented by the formula to within 1 per cent. The authors conclude that the difference in pressure of two isomeric substances at a given volume and temperature is of the same order as the deviation from Boyle's Law, and involves the second power of the density.

Mr. ROSE-INNES said the formula proposed was not an absolute solution of the problem, although it was the best of a large number which had been tried. It has been applied with success to Andrews's experiments on carbonic acid, and to experiments which have been made upon ether and hexane. In the latter case the range in volume was too small to afford a rigorous test of the value of the formula. The range in volume in isopentane was from 400·0 to 3·4, in normal pentane from 300 to 3·4, and in ether from 350 to 3·4. The temperature varied in different experiments from 40° C. to 280° C. Objections have been raised to the formula on account of the number of constants it contains, and its complexity. Mr. Rose-Innes pointed out that it was necessary to have a complex formula, as they were not dealing with a simple problem, but with the results of experiments which went so far below the critical temperature that the volume occupied was only 3·4 times as great as the space which would have been occupied by the molecules at their closest packing. The reader of the paper compared the proposed formula with formulæ of Clausius, Sutherland, and Tait, containing 4, 4, and 6 constants respectively, and, finally, with the original equation of Van der Waals applied to experimental results by Amagat. It was shown that the agreement was much closer and the range greater.

Prof. CALLENDAR expressed his interest in the wide applicability of the author's formula, and asked if any theoretical significance could be assigned to the various constants which appeared.

Mr. ROSE-INNES said the R of their formula was the R of the perfect gas equation, and that the l and e corresponded respectively to the β and α of the ordinary Van der Waals expression. So far as he knew the k and g were meaningless.

A paper "*On the Distribution of Magnetic Induction in a Long Iron Bar*," by Mr. C. G. LAMB, was postponed until the next meeting.

CORRESPONDENCE.

THE 32 EQUIVALENT AND ITS RELATION TO THE PERCENTAGE OF AVAILABLE SODA IN CAUSTIC SODA.

To the Editor of the Chemical News.

SIR,—In my letter in last week's CHEMICAL NEWS an error has crept into the equation showing the number of c.c. of English test-acid required to neutralise 4·1 grms. of caustic soda. Instead of "$\frac{4·1 \times 100}{4·0} = 100·61$," it should, of course, be "$\frac{4·1 \times 100}{4·075} = 100·61$."—I am, &c.,

JOHN PATTINSON.

75, The Side, Newcastle-upon-Tyne,
May 30, 1899.

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CHEMICAL NOTICES FROM FOREIGN SOURCES.

Note.—All degrees of temperature are Centigrade unless otherwise expressed.

Comptes Rendus Hebdomadaires des Séances, de l'Académie des Sciences. Vol. cxxviii., No. 18, May 1, 1899.

A Double Carbonate of Potassium and Peroxide of Cerium.—André Job.—In a former paper, the author has shown that it is possible to peroxidise cerium in aqueous solution, and to maintain it in the peroxidised state in a stable form. Perceric solutions of potassium carbonate, prepared by peroxide of hydrogen, were so kept for several months. The present paper contains an account of the method of isolating the contained perceric salt. The solution is slowly evaporated at the ordinary temperature until crystals of an intense blood-red are deposited, which attain the length of about half a centimetre. These crystals on examination are found to belong to the triclinic system. This fact, in itself, is enough to show the presence of a new chemical compound, since none of the known substances obtained from the same solution crystallise in this system. The author has prepared these crystals in a state of purity, analysis showing them to be a well-defined double carbonate of potassium and peroxide of cerium having the formula $(CO_3)_3Ce_2O_3.4CO_3K_2.12H_2O$.

Supposed Fluorine contained in certain Mineral Waters. — F. Parmentier. — Fluorine or its compounds has been believed to be present in the waters of Mont Dore and Saint Honoré les-Bains, by the fact that after a time the glasses in which the waters are served become opaque—having the appearance of being etched by hydrofluoric acid. The waters in question are very rich in silica, which is often deposited on the surface at the source; they contain also bicarbonates of the alkalis and alkaline earths. The author has examined them carefully, and finds no presence of fluorine compounds in the water, but proves that the etched appearance of the glass is due to a very adhesive deposit of silica, and not to a fluorine compound. In many analyses of the waters of Mont Dore, no trace of fluoride of calcium was found.

Oxidising Power of Alkaline Periodates. — E. Péchard. — The author's experiments show that the periodates in alkaline or neutral solution have an oxidising effect on methyl-orange which is not possessed by iodates under the same conditions. In acid solution there is the same difference: peroxide of hydrogen decomposing periodic acid, whilst it has no effect on iodic. To explain these facts it must be assumed that these salts have a different constitution from the iodates and also from the perchlorates, which latter salts give none of the reactions mentioned above. The periodates, and in particular the salt $NaIO_4$, is able to liberate oxygen with analogous properties to that of ozone, and further investigation of the action of this salt on potassium iodide, iodine being liberated, confirms this theory.

Displacement of Mercury by Hydrogen.—Albert Colson.—(*a*) The action of hydrogen on a uniformly pulverised mercury compound is proportional to the weight of the solid. (*b*) The rapidity of absorption of hydrogen gas is not proportional to the mass—that is to say, to the pressure. In slow reactions it appears to be proportional to the molecular distance, *i.e.*, to the cube-root of the pressure. The author proves the above two statements by experiment. He also investigates the action of hydrogen on mercuric and mercurous salts. At 100° hydrogen has no action on corrosive sublimate, but reduces mercuric sulphate and nitrate. Powdered and dried mercurous nitrate slowly evolves nitrogen dioxide in presence of hydrogen at 100°:—

$$(NO_3)_2Hg_2 + 4H = 2NO + 2HgO + 2H_2O.$$

Luminous Phenomena produced by the Action of certain Ammonium Salts on Fusing Potassium Nitrite.—D. Tommasi.—If a crystal of ammonium chloride is thrown into fusing potassium nitrite, the crystal assumes the form of a brilliant globule, which becomes incandescent, then burns and disappears with a feeble detonation. If sulphate of ammonium is used instead of the chloride, the luminous effect is more intense. Ammonium nitrate, in contact with fusing potassium nitrite, produces the most remarkable of the luminous phenomena. If nitrate is used in the state of crystalline powder, a series of phosphorescent spots are noticed on the surface of the bath of potassium nitrite, but if a crystal is used, it immediately forms an incandescent globule surrounded by a phosphorescent ring having a very rapid circular motion. After a few seconds it disappears, burning with a violet flame.

Morphine and its Salts.—Emile Leroy.—The author's experiments show that morphine precipitated by KOH or NH_3 is identical with morphine crystallised in the hydrated state. In fact, it is observed during the experiments that the evolution of heat is not instantaneous, but is produced during two or three minutes, which shows that morphine set free by an alkali undergoes a progressive transformation, which tends finally to the crystalline state.

Racemisation of Camphor.—A. Debierno.—Ordinary active camphor can be completely racemised without using the high temperature which was believed to be necessary. The author obtains this result by acting upon the molecular combination which forms camphor with aluminium chloride.

Tetramethylated Disymmetric Derivatives of Diamidodiphenylethane.—A. Trillat.—Disymmetric tetramethyldiamidodiphenylethane can be prepared by using, instead of pure acetic aldehyde, a mixture of alcohol and acetal, such as can be obtained by oxidising ethyl alcohol by potassium bichromate and dimethylaniline. The acetal decomposes, forming acetic aldehyde, which combines with the dimethylaniline—

$$CH_3.CH\begin{matrix}<^{C_2H_5O}\\<_{C_2H_5O}\end{matrix} + 2C_6H_5N(CH_3)_2 =$$

$$= CH_3.CH\begin{matrix}<^{C_6H_4N(CH_3)_2}\\<_{C_6H_4N(CH_3)_2}\end{matrix} + 2C_2H_5OH.$$

Berichte der Deutschen Chemischen Gesellschaft. Vol. xxxi., July 25, 1898.

Formation of Methane-disulphonic Acid during the Reaction of Fuming Sulphuric Acid on Acetylene. — W. Muthmann. — Methane-disulphonic acid, $CH_2(SO_3H)_2$ can be easily obtained by passing a slow current of acetylene through cold fuming sulphuric acid containing 80 per cent of anhydride. It is then thrown into iced water, saturated with $BaCO_3$, filtered, and evaporated. The barium salt is deposited on cooling in the form of flakes containing $2H_2O$. The free acid is in deliquescent needles; the ammonium salt is anhydrous, in the form of very soluble clinorhombic prisms; the potassium salt is analogous to the last.

Methylanilide of Malonic Acid.—D. Vorlaender and P. Herrmann. — Malonylmethylaniline is prepared by heating a mixture of 30 grms. of malonamide and 150 grms. of methylaniline up to 200—240° on an air-bath for six hours. The excess of the base is carried off by a current of steam and the residue is crystallised in ether. The return is 50 grms. Malonylmethylaniline crystallises in tabular prisms fusible at 109°, soluble in alcohol and boiling water, insoluble in HCl. Sodium reacts on a dry benzenic solution of this body, giving rise to a soda derivative soluble in benzene. If this solution is treated with the calculated quantity of iodine, methylaniline of ethanetetracarbonic acid is obtained in the form of white prisms, soluble in alcohol, benzene, and chloroform, and fusible at 231°.

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MEETINGS FOR THE WEEK.

MONDAY, 5th.—Royal Institution, 5. General Monthly Meeting.
—— Royal Institution. Centenary Day.
—— Society of Chemical Industry, 8. "A New Method for the Analysis of Commercial Phenols," by Dr. S. B. Schryver. A Demonstration of Printing by Electricity without the Aid of Rollers or Ink, by Dr. S. Rideal, F.I.C. "Notes on Cacao Butter," by Dr. J. Lewkowitsch, F.I.C. "The Use of Iron as the Active Element in Primary Batteries used for Electrolysing," by Col. J. Waterhouse, I.S.C.

TUESDAY, 6th.—Royal Institution, 3. Commemoration Lecture by Professor Lord Rayleigh, F.R.S. H.R.H. The Prince of Wales, K.G., Vice-Patron, presiding. Evening Reception by the Lord Mayor to the Members, Foreign Guests, and Representative Men, at the Mansion House.

WEDNESDAY, 7th.—Royal Institution, 9. Commemoration Lecture by Professor Dewar, F.R.S. His Grace the Duke of Northumberland, K.G., President, presiding.
—— Society of Public Analysts, 8. "On some Comparative Analyses of, and Digestive Experiments with White and Whole-meal Breads," by Otto Rosenheim, Ph.D., and Phillip Schidrowitz, Ph.D. "Note on Coffee Extracts," by C. G. Moor, M.A., F.I.C., and Martin Priest. "On the Determination of the Iodine Value," by J. Lewkowitsch, Ph.D., F.I.C. "On the Influence of Ammonium Salts on the Precipitation of Nickel by Ammonia," by Arthur Marshall.

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Wanted, Demonstrator of Chemistry (illness substitute) in London immediately. Duties about ten or twelve hours per week for six weeks.—Replies, stating qualifications and salary required, to "Demonstrator," CHEMICAL NEWS Office, 6 & 7, Creed Lane, Ludgate Hill, London, E.C.

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THE CHEMICAL NEWS.

Vol. LXXIX., No. 2063.

THE CRYSTALLINE STRUCTURE OF METALS.*

By J. A. EWING, F.R.S.,
Professor of Mechanism and Applied Mechanics in the University of Cambridge,
and W. ROSENHAIN,
1851 Exhibition Research Scholar, Melbourne University.

In a previous communication read to the Society on March 16, a preliminary account was given of some of the results the authors had arrived at in studying metals by the microscopic methods initiated by Sorby, and pursued by Andrews, Arnold, Behrens, Charpy, Osmond, Roberts-Austen, Stead, and others. The present paper deals with a development and extension of the same work. It relates chiefly, though not exclusively, to the effects of strain, and the relation of plasticity to crystalline structure.

It is well known that the etching of a polished surface of metal reveals, in general, a structure consisting of irregularly shaped grains, with clearly marked boundaries. Each grain is a crystal, the growth of which has been arrested by its meeting with neighbouring grains. This view, as Mr. Stead has pointed out, is strongly supported by the appearance of the etched surface under oblique illumination, when the several grains are seen to reflect light in a way which is consistent only with the idea that on each there is a multitude of facets with a definite orientation, constant over any one grain, but different from grain to grain. The formation of such a structure is well exhibited, on a relatively enormous scale on the inner surface of a cake of solidifying bismuth, from which the still molten metal has been poured away. Another striking example of this structure is seen in steel containing about 4¼ per cent of silicon. The fractured ingot of this material exhibits large crystals, and by deeply etching a polished surface Mr. Stead has obtained a beautiful development of the regularly oriented elements of which the crystalline grains are built up (*Journ. Iron and Steel Inst.*, 1898) on a scale so large as to require but little magnification.

The authors have obtained much evidence that this structure is typical of metals generally. Probably under no condition does any metal cease to be crystalline.

The crystalline character of wrought iron bars or plates is seen when the polished surface is etched, not merely by the general appearance of the grains under oblique light, but by the development of geometrical pits on the surface. These pits have a definite orientation over each grain, and the orientation changes from one grain to another. Usually in the purest commercial iron their outline is that of plane sections of a cube, but occasionally they are apparently plane sections of an octahedron. In some instances isolated and comparatively large pits only are seen; in others nearly the whole surface of a grain, when viewed under a magnification of 1000 or 2000 diameters, is found to be covered with small as well as large pits, geometrically similar and similarly oriented. Photographs of these are given in the paper.

For the purpose of producing smooth surfaces in the more fusible metals, without polishing, the metal was poured in a molten state on a plate of smooth glass. The surface produced in this way shows well the boundaries between the grains, and in some cases it also exhibits the crystalline character of the grains in a remarkable way by means of geometrical pits, which are apparently formed on the surface in consequence of the presence of small bubbles of air, or, more probably, of gas given out from the metal itself during solidification. Cadmium shows these particularly well, and they are to be observed also in tin and zinc. These air-pits are seen, under 1000 diameters, to be negative crystals, similar and similarly oriented on each grain, and, in cadmium, to have outlines which suggest that they are sections of hexagonal prisms. Their characteristics are exhibited in the photographs, which also show how the boundaries between the grains are emphasised by the collection there of air or of gas given off by the metal during solidification. The true boundary is merely the trace of a surface on a plane, but it may be broadened out in this way into a wide shallow channel. The effects of strain have been examined in many metals, using surfaces prepared either by polishing or by casting against a smooth plate. When any metal is strained beyond its elastic limit in any way, the surface of each crystalline grain becomes marked by one or more systems of lines running in a generally straight and parallel fashion over it. The direction of the parallel lines changes from grain to grain. Thus these lines serve to mark out one grain from another in a metal which, although polished before straining, has not been etched to develop the boundaries. As straining proceeds, the lines become more and more numerous and emphatic, and two, three, or four systems appear on each grain.

The nature of these lines has been described in the authors' paper of March 16. They are slips along cleavage or gliding planes in the crystals. The effect of each slip is to develop a step on the polished face. The short inclined surface forming this step looks black under vertical illumination, but shines out brightly when oblique light of a suitable incidence is used. These slip bands, as they were named in the previous paper, are thus seen as narrow dark or bright bands, according to the nature of the lighting.

The authors have developed slip-bands in iron, copper, gold, silver, platinum, lead, tin, bismuth, cadmium, aluminium, nickel, as well as steel, brass, gun-metal, and various other alloys. So far as the observations go, they occur in all metals.

The slip-bands are in themselves an evidence of crystalline structure, and, further, they show how such a structure is consistent with plasticity, and how it persists after plastic strain has occurred. The "flow" or non-elastic strain of a metal occurs through numerous finite slips taking place on the cleavage or gliding surfaces in each of the crystalline grains of which the metal is an aggregate. The elementary pieces which slip on one another retain their primitive crystalline character.

Further, if the movement of the pieces with respect to each other in any one grain is a movement of translation only, their orientation should remain uniform in each grain.

That this is actually the case is demonstrated by examining specimens of metal which had been violently deformed without any subsequent annealing or heating. In metal that has been rolled or hammered in the cold state, or deformed by tension or compression or strain of any kind, however severely, the grains are still seen where a surface is polished and etched. Their form is much changed by the strain which the piece has undergone. But the fact that they have retained their crystalline structure is demonstrated when, after polishing, the piece is subjected to a slight additional strain of any kind, for the effect of this additional strain is to develop slips of the same general character as before. Further evidence to the same effect is given by the fact that etching the polished surface of a very severely strained piece develops geometrical pits, which are similar and similarly oriented over the face of each grain, notwithstanding the great distortion which the grain has suffered as a whole. The effects of oblique lighting in metal which is polished and etched after severe straining are referred to as illustrating the same point. The persistence of crystalline structure

* Abstract of the Bakerian Lecture read before the Royal Society, May 18, 1899.

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is demonstrated by micro-photographs of the section of a bar of Swedish iron which had been rolled cold from a diameter of ⅞ inch to a diameter of ½ inch without subsequent heating. The outline of the grains is much distorted, but the orientation of the crystalline elements remains constant within each individual grain.

The slips in metals which exhibit a cubical crystalline structure on etching are in some instances parallel to the faces of the cubes, and are very frequently inclined to the faces, apparently along the octahedral planes. Stepped lines are frequently seen, and also lines which appear curved probably in consequence of numerous steps which are unresolved even under the highest powers. In exceedingly plastic metals, such as lead, copper, and gold, the lines are particularly straight. A piece of lead cast against glass to produce a smooth surface gives, when slightly strained, a splendid display of slip-bands, and the boundaries of the grains are sharply defined by the meeting of the lines on one grain with those on its neighbours. Another way to get a clear lead surface for the purpose of showing slip-bands is to press a freshly-cut piece of the metal with considerable force against a smooth object. Photographs of slip-bands in iron, gold, silver, lead, copper, and other metals are given in the paper.

When a metal is fractured the grains do not as a rule part company at their boundaries, but split along cleavage surfaces. It is to this that the crystalline appearance, obvious in many fractures, is due.

In several metals the authors find that "twinning" takes place in the crystalline structure as an effect of strain. Samples of copper, which in the original cast state gave no evidence of the existence of twin crystals, were hammered or otherwise wrought, and were then found to be full of twins. The twinning produced in this way survived after the wrought copper had been raised to a red heat and allowed to cool. Similar results were obtained in gold and in silver; the metal in the cast state did not show twins, but they were found after the metal had been wrought and subsequently softened by annealing. An example of twinning was observed in nickel after the application of a somewhat severe strain. Twins were readily developed in cadmium by strain, apparently as a result of the slight strain which was applied for the purpose of developing slip-bands. They were also found in lead, zinc, and tin, either as a primitive feature in the crystallisation or produced by straining. The twinning frequently takes the form of a large number of parallel bands within a single grain, and a twin band due to strain in one grain is sometimes associated with a twin band in neighbouring grains, the bands being continuous except for a change in orientation in passing from grain to grain.

Photographs of twin bands in copper, gold, lead, and other metals are given, showing the twin bands as revealed by a cross-hatching of parallel slip-lines, the sets of lines being parallel to one another in alternate bands of the twin. The twinning under strain which we have observed in various metals is similar to that which is known to occur in calcite. It may be regarded as a result of slip accompanied by a definite and constant amount of rotation on the part of the molecules.

From this point of view there are two modes in which plastic yielding occurs in a crystalline aggregate. One is by simple slips, where the movements of the crystalline elements are purely translatory and their orientation is consequently preserved unchanged. The other is by twinning, where rotation occurs through an angle which is the same for each molecule in the twinned group. Both modes are often found not only in a single specimen of metal but in the same crystalline grain.

At the suggestion of Messrs. Heycock and Neville, the authors' examination of the effects of strain has been extended to certain eutectic alloys. The structure of such alloys has already been described by Osmond, with whose observations these are in agreement. The alloy generally exhibits rather large grains, the structure of which is very different from that of pure metals, for it consists of an intimate intermixture of two constituents, one of which appears as separate or dendritic crystals on a field formed of the other constituent. The two are seen forming an exceedingly minute and complex structure within each of the large grains of which the alloy is made up. Straining has the effect of making this intimate structure more apparent, by causing slips which set up differences of level between pieces of one and the other constituent.

A study of the micro-structure of alloys suggests a possible explanation of the peculiarities they present in regard to variation of electrical conductivity with temperature. The two constituents may behave individually as pure metals in this respect, but if their coefficients of expansion are different the closeness of the joints between them will depend on the temeprature. Thus if the more expansible metal exists as plates, or separate pieces of any form within the other, the effect of heating will be to make the joints between the two conduct more readily, with the result of reducing the increase of resistance to which heating would otherwise give rise, and in extreme cases with the effect even of producing a negative temperature coefficient. The high resistance of alloys generally may be ascribed to the large number of joints across which the current has to pass.

In casting metals against glass and other smooth bodies for the purpose of getting a surface fit for microscopical examination, a surface is occasionally produced which not only shows the true boundaries between the crystalline grains, but also additional markings which simulate boundaries in a very curious manner. These pseudo-boundaries are often polygonal in form, like the real boundaries, and have an intimate geometrical association with them. Under low powers they are in some instances difficult to distinguish from true boundaries; but the distinction is apparent under high powers, and it becomes obvious as soon as slip-bands are developed by the straining of the metal. The pseudo-boundaries are found to consist in small variations of level in the surface of the grains in which they occur. Their form suggests that they are projections upon the surface of real edges below. They occur very conspicuously in cadmium, especially when it is cast on a cold surface, and less conspicuously in zinc. It is probable that in the strain set up by unequal cooling after the metal has solidified, the lower edges of the crystalline grains project a sort of image of themselves on the surface by slips, or possibly by narrow bands of twinning. The effect resembles that of a Japanese "magic" mirror, in which slight inequalities of the surface, corresponding to a pattern behind, cause light reflected from the mirror to produce an image in which a ghost of the pattern may be traced.

The authors regard their experiments as establishing the conclusion briefly stated in their previous paper, to the effect that the plasticity of metals is due to the sliding over one another of the crystalline elements composing each grain, without change in their orientation within each grain, except in so far as such change may occur through twinning.

ON A TUNGSTO-POTASSIC TUNGSTATE.

By L. A. HALLOPEAU.

I HAVE already (*Bull. Soc. Chim.*, Series 3, vol. xix., 745) established the fact that hydrogen reduces paratungstate of potassium, giving a compound with the formula $K_2O,WO_3+WO_2.WO_3$.

We obtain a tungsten bronze, of a different composition, by the reduction of the acid tungstate of potassium by tin. The experiment is performed very easily by heating paratungstate of potassium for an hour with a small quantity of tin. The operation should be carried out in a porcelain crucible in a muffle furnace, heated to

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a temperature high enough to melt the tungstate. The melted mass is treated successively with boiling water, concentrated hydrochloric acid, and a boiling solution of carbonate of potassium at 50 per cent. After a final washing with warm water, a pulverulent substance remains having a very deep blue colour. Under the microscope we see that this matter is composed of prismatic crystals; they answer to the formula $K_2O,WO_3 + WO_2,3WO_3$. By its constitution this body resembles the tungsto-lithic tungstate $Li_2O.WO_3 + WO_2.3WO_3$, which I have already described in a previous paper (*Bull. Soc. Chim.*, Series 3, vol. xix., p. 953), and the tungsto-sodic tungstate, $Na_2O.WO_3 + WO_2\,3WO_3$, which occurs in blue prismatic crystals like the preceding ones, and which was obtained by Philipp by fusing the acid tungstate of sodium with tin for a short time. In preparing this substance care must be taken not to prolong the action of the tin on the melted acid tungstate.

Philipp has shown that if we keep the tin in the presence of fused acid tungstate of soda for a sufficiently long time, we no longer obtain the same compound. It is Wohler's salt which is formed, $Na_2O.WO_3 + WO_2.WO_3$. This fact has already been observed by Wright.

On carefully examining the tungsto-potassic tungstate prepared by means of tin, we also observe here and there a few violet-red prisms, similar to the crystals obtained by reduction by hydrogen, but they are in excessively small quantity. I have in vain tried to obtain a greater proportion of them by prolonging the action of the tin on melted paratungstate of potassium. If the duration of the experiment is increased a total reduction of the potassium salt takes place: after six hours' heating, I found a greyish powder formed of a mixture of metallic tungsten and of crystallised binoxide of tin.—*Bull. Soc. Chim.*, Series 3, vol. xxi., No. 6.

THE VOLUMETRIC ESTIMATION OF CARBON.

By HENRI IMBERT and P. COMPAN.

We undertook the following experiments with a view to the estimation of the pure carbon deposited in very thin layers on sheets of glass.

The process depends on the following facts:—

A sulphuric solution of chromic acid oxidises carbon, giving carbonic acid and chromic sulphate. By disregarding the sulphuric acid we can represent the reaction by the formula—

$$(1).\quad 3C + 4Cr_2O_3 = 2Cr_2O_3 + 3CO_2,$$

from which it follows that 36 of carbon corresponds to 400 of chromic acid reduced. Again, a sulphuric solution of chromic acid acts on iodide of potassium in excess, setting iodine at liberty according to the equation—

$$(2).\quad 2CrO_3 + 6KI + 3H_2O = Cr_2O_3 + 6KOH + 3I_2.$$

100 of CrO_3 sets free $3 \times 127 = 381$ of iodine, which can be titrated by means of hyposulphite of soda.

Extremely small quantinies of carbon can be estimated by this process.

We operated in the following manner:—

A known weight of carbon, placed in a beaker, is treated with a known excess of a titrated solution of chromic acid, and a little sulphuric acid at 4 per cent; the solution is first evaporated on a sand-bath, then—when it is brought to a small volume—on a water-bath.

The colour does not appear to be modified until the liquid takes a syrupy consistence, but at this moment it shows a yellow to a greenish-yellow tint (a decided greenish-blue tint indicates that the quantity of chromic acid used is insufficient); under these conditions the carbon is entirely consumed. The residue, diluted with water, is then placed in a glass bromine bulb; we add iodide of potassium in excess, and, if the iodine is not set at liberty, a further quantity of sulphuric acid at 4 per cent is added. The liquid is exhausted four or five times with sulphide of carbon, which is collected in a glass-stoppered flask: when this exhaustion is complete, the sulphide of carbon remains colourless, and the supernatant liquid has a greenish-blue tint.

The sulpho-carbonic solution of iodine is agitated with bicarbonate of soda at 5 per cent, to neutralise the free sulphuric acid, and then titrated by means of hyposulphite of soda with the usual precautions.

From the volume of hyposulphite employed we deduce the chromic acid remaining, and, by difference, that used. According to equation (2) we calculate the weight of carbon which has been consumed.

We have operated on successive weights of carbon of 0·018, 0·040, and 0·025 grm., and have found 0·0171, 0·0388, and 0·02422 grm.

This carbon was prepared by the deposition of lamp-black on a sheet of glass, which was subsequently washed with alcohol (Crova and Compan, *Comptes Rendus*, cxxvi., 707) to remove pyrogenous products; the concordance of the results shows that the carbon was practically pure.

This method is of very great sensitiveness; in operating on a solution of 3·81 grms. of hyposulphite of soda per litre, corresponding to 1·945 grms. of iodine, we can very easily recognise the complete decolouration of the sulphide of carbon to one drop: now 0·0111 grm. of chromic acid corresponds to 0·0423 grm. of iodine and to 0·001 grm. of carbon.

Between two successive operations carried out on the same volume of CrO_3, before and after reduction by carbon, 0·001 grm. of the former corresponded to a loss of 0·0423 grm. of iodine set at liberty, and consequently to a difference of 21·7 c.c. of hyposulphite used.

We then operated on a microscopic cover-glass, covered with a thin film of alcohol-washed lamp-black. The titrated solutions corresponded to the hyposulphite solution at 3·8 grms. per litre, and we were thus able to estimate 0·0013 grm. of carbon deposited. The sensitiveness of the method, in our opinion, enables us to accurately estimate 1 m.grm.

In devising this method we had to consider the estimation of chromic acid by the liberation of iodine, an iodide, and the titration of the iodine.

The results obtained corresponded very accurately with those obtained by ponderable means, by precipitation in the state of chromate of lead.

The facility with which the iodine is set free in the cold, by a sulphuric solution of chromic acid, has led us to effect the separation of bromine from iodine by this reagent. We operated successively on—

10 c.c. of a solution of iodine						
10	„	„	„	+ 10 c.c. of a solution of bromine		
10	„	„	„	+ 20	„	„
10	„	„	„	+ 30	„	„

The volume of the titrated solution of hyposulphite of soda necessary for the decolouration of the sulphide of carbon was 9·80 c.c. for each of these operations, no matter what excess of sulphuric and chromic acids was used. The bromine is, therefore, not set free under the conditions of the experiment; we simply experienced a little more difficulty in the exhaustion with the sulphide of carbon. It is not till after twenty-four hours after the separation of the iodine that the sulphide of carbon left in contact with the solution becomes coloured faintly yellow.

We therefore think that M. Carnot's process, recently described in the *Bulletin* (Series 3, xix., 251), might be modified by substituting, in the separation of the bromine and iodine, a cold sulphuric solution of chromic acid for the nitrous sulphuric acid.—*Bull. Soc. Chim.*, Series 3, vol. xxi., No. 6,

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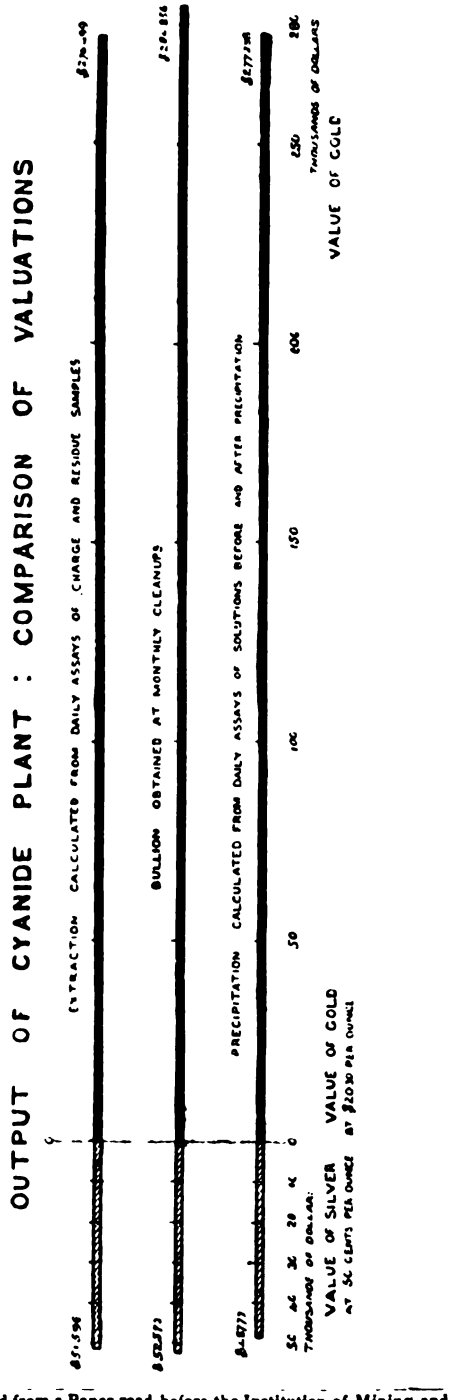
NOTES ON THE ALLEGED SHORTAGE IN CYANIDE BULLION.*

By C. W. MERRILL, Assoc. Inst. M.M.

THE impression that the bullion returns from cyanide plants are, in spite of the observance of all possible precautions, uniformly less than the correct tonnage multiplied by the difference between the values per ton indicated by assays of the "charges" and "residues," seem to have become so general that it was thought that the accompanying plan, with a brief explanation as to how the figures were computed, would be of interest.


OUTPUT OF CYANIDE PLANT : COMPARISON OF VALUATIONS
EXTRACTION CALCULATED FROM DAILY ASSAYS OF CHARGE AND RESIDUE SAMPLES
BULLION OBTAINED AT MONTHLY CLEANUPS
PRECIPITATION CALCULATED FROM DAILY ASSAYS OF SOLUTIONS BEFORE AND AFTER PRECIPITATION
VALUE OF GOLD
THOUSANDS OF DOLLARS
VALUE OF SILVER
AT 56 CENTS PER OUNCE
VALUE OF GOLD
AT $20·00 PER OUNCE

The figures are the results from the operations from July, 1897, to November, 1898, of the tailings plant of the Montana Mining Co., Ltd., the capacity of which is 12,000 tons per month.

About 125 truck-loads, of 3 tons each, are treated daily; from six to ten of these loads are weighed, and large samples taken from each; the accumulation of these car-moisture samples gives the average daily moisture sample. From the number of loads dumped, the average weight per load, and the moisture per cent, is calculated the number of dry tons treated daily.

The sand passes from the cars to the bins, and thence by belt conveyors into a rotary distributor over the centre of each vat. The stream of sand is sampled three times an hour for nine hours, the time taken to fill a 400-ton vat. This large sample is quartered down, and four assay tons of the dried sample are taken for duplicate melts and weighings of gold and silver. If the variation in the weights of gold obtained from these two melts does not exceed 1/50 m.grm., the average is taken as the value per ton of the tailings charged that day; otherwise the assays must be repeated.

After treatment, 16 cores are taken from the residue in the vat; this sample, weighing several hundred pounds, is in turn cored, giving about 20 lbs., which is dried, mixed, and quartered, for the final assay sample. If the final weighings differ by more than 1/50 m.grm., the assays must be repeated.

The monthly output calculated on the basis of the preceding determinations are shown in the upper line of the accompanying figure, the gold being to the right of the datum line, and the silver to the left.

The total amount of unprecipitated solution is measured, sampled, and assayed, as is also the precipitated solution. The solutions are evaporated down to a small bulk, a much larger quantity of the latter than of the former being taken; a mixture of litharge, silica, and charcoal added, and the whole heated till dry; after cooling, carbonate of soda is added, and the whole placed in a crucible, melted, and assayed. These solution assays are of great practical utility, not only as guides to the efficiency of the precipitation, but also as giving warning of the presence of reducing material in any charge several days before the residue from such a charge is available for assay; they are made primarily for these reasons.

The estimation of the values recovered monthly on the basis of these solution assays is shown on the lower line of the figure.

The monthly bullion assays are made with the usual precautions, including determination of the cupel absorption, check for volatilisation of silver, &c., and are shown in the centre line of the figure. A shortage of bullion is usual in the first clean-up, the deficiency being made up in the succeeding months.

The total value of gold and silver required by the daily assays is 328,096·21 dollars, and that actually recovered is 337,428·62 dollars, or an excess of 2·84 per cent over the estimate—a highly satisfactory concordance.

* Abridged from a Paper read before the Institution of Mining and Metallurgy, April 19, 1899.

Ratio of the Atomic Weights of Hydrogen and Oxygen.—A. Leduc.—The synthesis of water by weight has led the author to the conclusion that 15·88 is the exact relation between the atomic weights of oxygen and hydrogen. Another method, founded on the determination of the densities of the two gases (both separate and mixed together in the proportion to form water), has given a result (15·868) distinctly lower than that given above. This latter result is probably due to the increase of pressure produced when 2 vols. of H are mixed with 1 vol. of O.—*Comptes Rendus*, cxxviii., No. 19.

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THE DETERMINATION OF POTASH AS PERCHLORATE.*

By F. S. SHIVER.

The increasing use of potash salts for fertilising purposes has made the determination of potash a question of prime importance to the agricultural chemist.

The desire to devise a method at the same time rapid and accurate has been manifested in many ways in the past few years, especially in Germany, the seat of the great potash deposits.

The German chemists believe they have solved the problem in the so-called Stassfurt method, which, as all know, permits of the separation of the potash by platinum chloride after previous precipitation of sulphuric acid by barium chloride in slight excess, and in a strongly acid solution. This method, with practice, is quite accurate and rapid, with a slight tendency, however, to high results in my hands. It possesses little advantage over the Lindo-Gladding method, in so far as rapidity and accuracy are concerned.

The following determinations were made by the Stassfurt method—potassium sulphate, C.P., and potassium chloride, C.P., were mixed with such impurities as to imitate the composition of commercial sulphate of potash, sulphate of potash and magnesia, kainit, and muriate.

Table I.

	K_2SO_4 used. Grm.	K_2SO_4 found. Grm.	Error on K_2SO_4. Grm.	Error on K_2O. Grm.
Sulphate of potash	0·3284	0·3291	+0·0007	+0·0004
		0·3289	+0·0005	+0·0003
Sulphate of potash and magnesia ..	0·1856	0·1863	+0·0007	+0·0004
		0·1870	+0·0014	+0·0008
Kainit	0·1000	0·1003	+0·0003	+0·0002
		0·1009	+0·0009	+0·0005
	KCl used. Grm.	KCl found. Grm.	Error on KCl. Grm.	Error on K_2O. Grm.
Muriate	0·2506	0·2498	−0·0008	−0·0005
	0·2522	0·2514	−0·0008	−0·0005

The factor used for converting potassium platinichloride into potassium sulphate was 0·35694, which is practically the same as that recommended in the Stassfurt method, viz., 0·357. The factor used for converting potassium platinichloride into potassium chloride was 0·30557, which is practically the same as that recommended in the Stassfurt method, viz., 0·3056. It will be seen from the above results that the method is quite accurate, with a tendency, however, to slightly high results.

In view of the increasing importance of the potash determination, it is highly desirable that we should possess a check method, rapid and accurate, based on some other principle of separation than that with platinum chloride.

All of our present methods for the determination of potash involve the use of platinum chloride as a means of final separation, and hence they are all subject to the same general sources of error, such as solubility of the platinichloride in the 80 per cent wash alcohol used, &c.

Of all the salts which potassium forms with acids, none are as well adapted for furnishing the basis of another process as the perchlorate, which is nearly insoluble in strong alcohol.

As all the compounds which perchloric acid forms with the bases other than potash and ammonia are soluble in alcohol, we may readily deduce the basis of another process. The determination of potash as perchlorate is an old process due to Sérullas, who first noticed the insolubility of the salt in alcohol, and to Schlœsing, who made it the basis of a new process. Schlœsing's process, improved later by Kraut, has, however, not come generally into use, since the same produces inaccurate results.

W. Wense (*Zeit. Angew. Chem.*, 1891, 691; and 1892, 233) has made the process useful, since he diminishes the solvent action of the alcohol on the perchlorate through the addition of slight quantities of perchloric acid. He describes the following course of procedure:—

The solution to be investigated is evaporated, after once freeing it of sulphuric acid and non-volatile acids with perchloric acid in a porcelain dish. In order to wash the perchlorate easily, it is desirable to produce the same in a granular condition. This is attained by warming the solution containing the potash on a water-bath before adding the perchloric acid, which must be run in drop by drop. In all cases there are used about one and a half to one and three quarters times the amount of perchloric acid necessary for the decomposition of the salt present.

After the addition of the perchloric acid, the solution is evaporated until all odour of hydrochloric acid or other volatile acids has disappeared. For washing the precipitate 96 per cent alcohol is used, to which two-tenths per cent of its weight in perchloric acid is added.

The residue from the evaporation is treated with 10 c.c. of the alcoholic wash solution, which may take up only 1/20,000th of a part of potassium perchlorate, and the salt mass is then broken up with a stirrer.

Decantation is performed through a weighed filter, which has been previously dried at 120—130° C., when the breaking-up of the salt mass is repeated, and the residue again treated with the alcohol wash solution. The precipitate is then brought on the filter, and freed of the adhering perchloric acid solution by washing with a few c.c. of pure alcohol. The filter is then pressed between folds of filter-paper, dried for twenty-five minutes at 120—130° C., and weighed.

One part of potassium perchlorate corresponds to 0·5382 part of potassium chloride, and 0·6289 part of potassium sulphate.

According to the author, the whole washing with a good pump occupies only a short time, and requires 50 to 70 grms. of alcohol. If the substance to be investigated contains sulphuric acid, the same is to be removed in the usual way by barium chloride previous to the determination of the potash. The author, who used the method in the investigation of potassium chloride, C.P., commercial muriate, kainit, and carnallite, obtained—according to the analyses reported—very favourable results.

R. Caspari (*Zeit. Angew. Chem.*, 1893, 68) recommends collecting the potassium perchlorate in tubes containing asbestos filters, and subsequent drying for twenty minutes at 130—150° C. The tubes are allowed to cool in a desiccator or in the air and then weighed.

According to Caspari, the method is applicable for fertilisers, ashes, and the like, in the presence of phosphoric acid, alkaline earths, iron, alumina, and manganese, if the following method of procedure is adopted:—

After the removal of sulphuric acid, the hydrochloric acid solution is evaporated for the purpose of getting rid of the free acid, the residue stirred with 20 c.c. of hot water, after which perchloric acid is added in quantity not less than one and a half times that necessary for the decomposition of all salts present.

The solution is now evaporated with frequent stirring to a syrupy consistency, some hot water is again added, and the solution evaporated still again with occasional stirring until the disappearance of all odour of hydrochloric acid, and till the appearance of white fumes of perchloric acid. An evaporation of large quantities of perchloric acid is to be avoided; if this takes place, more perchloric acid is to be added.

The cooled, more or less syrupy, contents of the dish are well stirred up with about 20 c.c. of wash alcohol (96 per cent alcohol containing two-tenths per cent perchloric acid), taking care, however, not to reduce the potassium perchlorate to a fine powder. After the alcoholic solution has become clear, it is decanted through the asbestos

* *Journal of the American Chemical Society*, xxi., No. 1.

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filters, the washing repeated with the same quantity of wash alcohol, allowed to settle, and decanted again.

The residue remaining in the dish is freed of alcohol by gently warming, evaporating again with about three-tenths grm. of perchloric acid and a little water, and washing the cooled mass with several c.c. of alcohol, with which it is also brought into the filters and the perchlorate in the tubes finally covered with a little pure alcohol. The potassium perchlorate obtained in this way contains, according to Caspari, no phosphoric acid, or only slight quantities of the same; on an average only 0·00057 grm. phosphoric acid.

In the separation of sulphuric acid, Caspari seeks to avoid, as much as possible, a loss of potash, since he precipitates in a strong hydrochloric acid solution at the boiling temperature with a concentrated solution of barium chloride made acid with hydrochloric acid. Experiments of the author prove also the applicability of the method in the presence of other acids not volatile on the water-bath, as chromic acid, and also boric, tartaric, and oxalic acids. If ammonium salts are present, they are to be removed either with soda-lye or milk of lime, by gentle heating or through careful ignition.

A. Kreider (*Am. Journ. Sci.*, xlix., 443) has followed the method as described by Caspari, and has obtained very satisfactory results. Kreider found the Gooch crucible preferable in the filtering of the perchlorate, and recommends the same instead of the tubes proposed by Caspari. In the presence of phosphoric acid, the previous separation of which is not necessary, it appeared advisable, according to Kreider's experiments, to allow the perchlorate precipitate to stand with an excess of perchloric acid before treating with alcohol.

Six determinations made of potassium unmixed with other bases or non-volatile acids gave the following results:—

In two cases the theoretical amount of potash (K_2O) was recovered as perchlorate; in three cases there was a loss of 0·0002 grm.; and in one case a loss of 0·0003 grm.; one-tenth grm. of potassium chloride was operated on in all cases. In order to repeat Kreider's work, and to ascertain the accuracy of the process, the following work was undertaken. A solution of chemically pure potassium chloride was prepared by dissolving 1·0005 grms. in 200 c.c. water. 1 c.c. of the solution was found to contain 0·005 grm. potassium chloride, aliquot portions being measured from a burette, evaporated, dried, and weighed.

In all the work here reported, the method as proposed by Caspari, with the use of the Gooch crucible, as suggested by Kreider, was employed.

However, in the first three experiments reported, the perchlorate was collected on paper filters as suggested by Wense, washed in the usual way, dried, and the perchlorate dissolved in hot water, and the solutions evaporated to dryness in platinum dishes and weighed.

In all cases the weighed perchlorate was a little discoloured, due to the fact that the paper filters had been acted on to a slight extent by the perchloric acid, causing them to char a little around the edges during the process of drying. In the subsequent leaching with hot water, some of this carbonaceous material dissolved, and went in solution with the perchlorate.

The results obtained by weighing in dishes as above described were as follows:—

TABLE II.

	KCl solution used. C.c.	Equivalent to KCl. Grm.	KCl found. Grm.	Error on KCl. Grm.	Error on K_2O. Grm.
I. ..	6·2	0·0310	0·0310	+0·0000	+0·0000
II. ..	8·1	0·0405	0·0411	+0·0006	+0·0004
III. ..	5·0	0·0250	0·0253	+0·0003	+0·0002
Average ..		0·0322	0·0325	+0·0003	+0·0002

It will thus be seen that the average error in these determinations is 0·0003 grm. KCl; it is possible that this slight plus error is due to the slight discolouration already noticed, and the weighing in dishes is not to be recommended, though the results obtained are sufficiently accurate for all practical purposes. In the other experiments which follow, the potassium chloride was weighed out directly for analysis, and the perchlorate was collected always in a Gooch crucible.

TABLE III.

	KCl used. Grm.	KCl found. Grm.	Error on KCl. Grm.	Error on K_2O. Grm.
I.	0·0848	0·0859	0·0011	+0·0007
II.	0·0217	0·0217	0·0000	0·0000
III.	0·0419	0·0413	−0·0006	−0·0004
IV.	0·1007	0·1009	+0·0002	+0·0001
V.	0·1003	0·1015	+0·0012	+0·0008
VI.	0·1016	0·1015	−0·0001	−0·0000
VII.	0·0217	0·0210	−0·0007	−0·0004
Average ..	0·0675	0·0677	+0·0002	+0·0001

In the above determinations No. 1 was among the first made, and it is possible that the slightly high results obtained were due to lack of familiarity with the method. Excluding No. I., the average would be as follows:—

KCl used. Grm.	KCl found. Grm.	Error on KCl. Grm.	Error on K_2O. Grm.
0·0647	0·0647	0·0000	0·0000

It would thus appear that the determination of potash as perchlorate in mixtures free from other bases and non-volatile acids, is quite accurate, equally as much as the determination by platinum salt.

After nitrogen and phosphoric acid, potash is the compound one has mostly to determine in fertilisers, plants, and soils. The potash is usually combined with sulphuric, nitric, or carbonic acid, and more rarely with phosphoric acid.

These salts are almost always associated with alkaline salts and the alkaline earths. It is now therefore a question of the applicability of the perchloric acid method to the determination of potash when associated with these other bases and non-volatile acids, such as sulphuric and phosphoric acid. In regard to the bases, it has been contended by some that magnesia is a disturbing element in the determination of potash by perchloric acid.

Schlœsing has shown, however, that in the following mixture, after the removal of sulphuric acid by barium chloride and conversion of bases into perchlorates, the magnesia did not have any disturbing effect.

Potassium chloride	0·0835 grm.
Magnesium sulphate	0·5740 ,,
Sodium chloride	0·1298 ,,
Calcium chloride	0·2330 ,,

In this mixture there was recovered, by proceeding as above stated, 0·0814 grm. potassium chloride. Kreider has also shown that magnesia has no disturbing effect. He treated 0·1500 grm. magnesium carbonate with perchloric acid, evaporated till fumes of perchloric acid appeared, and cooled, when magnesium perchlorate crystallised; on treating this with alcohol, a perfectly clear solution was obtained. It was also thought that it was necessary to remove all non-volatile acids previous to the separation of the potash as perchlorate. Caspari and Kreider have, however, shown that it is only necessary to remove sulphuric acid. In order to secure a nearly complete separation of phosphoric acid from the potassium, Kreider has shown that a considerable excess of perchloric acid should be left upon the potassium perchlorate before it is treated with the alcohol.

Kreider's results on a mixture containing—

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Potassium chloride	.. ..	0·1 grm.
Magnesium sulphate	.. ..	0·13 ,,
Aluminum sulphate	.. ..	0·05 ,,
Sodium phosphate	.. ..	0·4 ,,
Calcium carbonate	.. ..	0·13 ,,
Ferric chloride	.. ..	0·05 ,,
Manganese dioxide	.. ..	0·05 ,,

were quite promising, as will be seen from the results reported in the *American Journal of Science*, xlix., 448.

The method as modified by Caspari and Kreider is quite promising, and I hope in the near future to do some further work on the determination of potassium associated with other bases and non-volatile acids.

(To be continued).

PRESIDENTIAL ADDRESS TO THE IRON AND STEEL INSTITUTE.

By Professor Sir W. ROBERTS-AUSTEN, K.C.B., D.C.L., F.R.S.

(Concluded from p. 259).

1885-87. In no other branch of modern scientific literature than that of metallurgy does one individual stand far above his contemporaries and absolutely dominate his subject as does Dr. John Percy. It may be fairly claimed that he did this, for he truly represents the progress of metallurgical literature during the nineteenth centurv. He was also the century's greatest teacher; he found metallurgy practised in this country as an empirical art, His splendid works contain a record of its progress; his lectures at the Royal School of Mines secured it a scientific basis, and he trained a body of workers in whose hands the immediate future of metallurgy still, to a great extent, rests. To few men does the nation owe more than to our President of 1885-87. The educational work Dr. Percy began is being actively developed. As regards its progress in the future—which is of vital importance—there seem to me to be no requirements that may not be abundantly met by the extension of existing institutions. The establishment of a Board of Mining and Metallurgy in connection with the new Teaching University for London, would, I am satisfied, greatly sitimulate instruction in these subjects.

1887-89. Daniel Adamson will be known rather as a mechanical engineer, and the originator of the Manchester Ship Canal, than as a metallurgist. His Presidency of this Institute is, however, remarkable for his strenuous advocacy of the use, not only of steel as distinguished from iron, but that for definite purposes steel of a definite degree of carburisation and suitable composition should be employed. He also eloquently urged that the steel at all stages of its manufacture in its varied applications should receive suitable thermal treatment. He strongly advocated the use of steel for the manufacture of boilers, and he pointed out that by the use of steel rails and weldless solid rolled steel tyres, the saving to railway shareholders amounted to about £3,120,000 sterling per annum, while the safety and security of the travelling public had been correspondingly increased. No better indication of progress in the decade ending 1889 could well be given than this.

1889-91. The vast advance during the century in the applications of iron and steel in the manufacture of machinery, and more especially to locomotives, is fittingly represented by Sir James Kitson. We, moreover, owe him a deep debt of gratitude for the admirable way in which he represented the Institute by presiding at the Autumn Meeting of the Institute in Paris in 1899, as well as during the arduous but most remarkable visit to the United States in 1890. Sir James, by his unflagging vigour and unfailing tact, did much to cement the friendship of workers in iron and steel, both among our neighbours in France and our kinsmen in America. I will only add that he has persistently advocated the use, and has well maintained the reputation, of that admirable material, "best Yorkshire iron."

1891-93. One of the most noteworthy events in the metallurgical progress of this country was the acceptance by Sir Frederick Abel of the post of Chemist of the War Department. The teaching of such illustrious men as Berzelius, Heinrich Rose, and Liebig was just in process of thorough application in this country when Abel left our matchless teacher Hofmann to take his place among the earliest trained analytical chemists whose aid was sought by the ironmaster. He thus became, as it were, the "Patron" of works chemists. They are men on whose patient, monotonous, and often inadequately recompensed, labours the quality of British iron and steel has in no small measure depended, and I am glad to have this opportunity for offering my brethren, the chemists in works, a respectful tribute of admiration. The magnitude of their work may be gathered from the fact stated in the *Journal* of our Institute, that in one basic steel works over 110,000 determinations are made in a single year by three chemists and six assistants. Of Sir Frederick's numerous investigations, the one which appeals to us most closely is that which definitely settled, as Fe_3C, the composition of carbide of iron.

Lord Herbert of Lea, who was several times Secretary for War and was in office soon after Sir Frederick was appointed to Woolwich, appears to have been advised that "steel was wholly inapplicable for the manufacture of ordnance." When we consider what the nature of our present war material is, and reflect how large a part Abel played in its introduction and adoption, it will be evident that any further comments of mine as to the value of his labours would be unnecessary. He is himself a most active exponent of the truth "that the intimate blending of science with practice lies at the root of all industrial progress and success."

1893-95. I am quoting from an American source the testimony that "an historical sketch of the perfecting of modern processes of steel manufacture would afford the best glimpse that could be given of the career of Edward Windsor Richards." He was among the first to appreciate the need for reversing mill-engines, and an early one erected by him is still at work at Ebbw Vale. He designed the works of Messrs. Bolckow, Vaughan, and Co., at Middlesbrough, the largest in the kingdom, and as general manager of the famous Low Moor Works has fully maintained its reputation for the production of one of the most famous varieties of iron in the world. His connection with what is known as the basic process will be alluded to later on. In view of the fact that appliances will handle and forging presses deal with weights of steel up to 100 tons, he long ago anticipated the possibility of making 10 tons of steel into one ingot.

1895-97. The progress of an industry during the century can only be adequately indicated by the evidence afforded by statistics. In this respect no more comprehensive statements could have been desired than those embodied in the Presidential Address of Sir David Dale. Sir David has, however, secured a firmer claim to the gratitude of the nation than that which is derived from his powers as a statistician. He has from time to time been the trusted arbitrator between masters and men, and as Chairman of one Section of the Labour Commission (1891-94) rendered admirable services in the interests both of capital and labour. He was also the representative of this country at the Berlin Labour Congress of 1890. His work has, moreover, enabled us to trace, in the last twenty years of the century, the progress of the spirit of equity among all sorts and conditions of men, who have gladly borne testimony alike to his firmness and his justice. His efforts have been unwearyingly directed to removing difficulties which have from time to time arisen between employers and the employed. I need

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hardly allude to his long services as Treasurer of this Institute, nor do you need to be reminded that we owe the ability to carry on our work efficiently to his careful husbanding of our resources.

1897-99. To the foresight of Edward Pritchard Martin we owe the adoption in practice of one of the great processes which will render the nineteenth century memorable. I refer to what is collectively called the "Basic process." It would be impossible to trace its history now. I prefer in any reference, which must of necessity be so brief, to appeal to the appreciative words in the paper which Sidney Thomas and Percy Gilchrist communicated to our Institute in 1879. They then stated that, "on laying some of the first results obtained from this six-pound converter before Mr. Martin of Blenavon, he at once recognised their importance, and from that time we have been deeply indebted to him for his unfailing and consistent support and much valuable advice and assistance." It need only be added that the metallurgical world is also under a lasting debt of gratitude to Mr. Martin. Later on other aid was as gratefully recognised. Mr. Thomas said, on the occasion of his receiving the Bessemer Medal (1883), "the present position of dephosphorisation has only been rendered possible by the frank, generous, and unreserved co-operation of Mr. Windsor Richards, and of our earlier and consistent supporter Mr. Martin." All those I have named have received the Bessemer Medal. We lost Sidney Thomas far too soon. Mr. Snelus, to whose work I have already referred, and Mr. Gilchrist received the highest honour the scientific world has to bestow—the Fellowship of the Royal Society.

The introduction of labour-saving machinery in the great Dowlais Works, which Mr. Martin directs, marks an era in British metallurgy.

This concludes the list of those who have hitherto presided over this Institute, and it will have been evident that from time to time other interests than those connected with iron and steel have been represented by your Presidents. We were reminded of this fact when the Institute first met, now twenty-four years ago, at Manchester, where we are promised a delightful meeting again next autumn. The Bishop of that great city then welcomed us by a quotation from Virgil, which connects the age of iron with the age of gold. The passage runs thus:—

"quo ferrea primum
Desinet ac toto surget gens aureo mundo."

A President of this Institute who has had the privilege to serve in the Mint in a sense connects the iron and the golden age. I find that during the course of a long official career I have been responsible for the standard fineness of over one hundred and twenty-one millions of gold coin. This sum is so vast, and the anxiety connected with it has been at times so great, that I am not careful to conceal the pride revealed by this reference to it, as it is an exponent of the financial greatness of the nation which created the age of steel. But I value as highly the means of conducting research and the hope of being useful, which was also given me by the Government when I was appointed Professor of Metallurgy at the Royal School of Mines. I have in the discharge of my duties persistently striven to show that what is called applied science is nothing but the application of pure science to particular classes of problems.

I regret that space will not permit me to consider the progress of the century as measured by the work of our Bessemer Medallists. I hope, however, as regards the labours of the foreign recipients of the honour, to deal with them next spring. The metallurgy of America is so closely interwoven with our own, that I must permit myself a brief reference to four men who stand out from the industrial ranks of our kinsmen. These are Alexander Lyman Holley, the Hon. Abram S. Hewitt, John Fritz, and Professor Henry Marion Howe. All of them are Bessemer Medallists.

I only once had the good fortune to see the winsome pioneer of the Bessemer process in America, "our dear Holley," if I may borrow and adopt the phrase used to me by one of the American members at Stockholm last autumn, with reference to one the charm of whose character was neither impaired by difficulty or by success. All Holley did for the Bessemer process is fully recorded in our *Journal*, and it is only necessary to state that, from the time the first charge was blown at the Troy Works in 1865, there have been produced in America over sixty-one million tons of Bessemer steel.

It was in the works of the Hon. Abram S. Hewitt that the first Bessemer converter was installed, and Mr. Hewitt was also the first to build an open-hearth furnace in the United States.

Mr. John Fritz was one of the small band of leaders who so successfully developed the Bessemer process in the United States, and excited the admiration of the metallurgical world by large outputs from comparatively small installations. He also aided in designing one of the most important arsenals in the world, where the highest quality of open-hearth steel was produced.

Of the labours of my friend, Professor Henry Marion Howe, it would be difficult to speak adequately. As an experimental investigator he has greatly added to our knowledge of the properties of iron and steel. In the field of literature he has left on record a monumental work which enables him to rank with Dr. Percy as the metallurgical historian of the Anglo-Saxon race.

It may help us to estimate the value of the labours of the four men whose names I have given if we remember that at the present time the United States export about a million tons of iron and steel a year, while twenty years ago they were not exporting any. We may fairly consider, therefore, their influence on the rapid development of the United States navy. It would seem that we, in this country, in the belief in our insular security, had somewhat neglected the art of naval warfare, until Admiral Mahan reminded us of what we had done in the past, and of our possible course in the future, in a series of writings which have done much to convince the two nations, England and America, "that they are in many ways one."

It is time to offer a collective statement of the achievements which have either been actually effected or are in immediate prospect.

There are blast-furnaces which will produce 690 tons of pig-iron in twenty-four hours, with a consumption of little over 15·4 cwts. of coke per ton of iron. The gases from blast-furnaces are used not only as sources of heat, but directly in gas-engines.

There are Bessemer converters which can hold 50 tons of metal, and open-hearth furnaces which will also take 50 tons, while 100-ton furnaces are projected. The open-hearth furnaces are fed with 1 ton of material in a minute, by the aid of a large spoon worked by an electro-motor. There are gigantic "mixers," capable of holding 200 tons of pig-iron, in which, moreover, a certain amount of preliminary purification is effected.

Steel plates are rolled of over 300 feet in area and 2 inches thick. There are girders which justify the belief of Sir Benjamin Baker, that a bridge connecting England and France could be built over the Channel in half-mile spans. There are ship-plates which buckle up during a collision, but remain water-tight.

There are steel armour piercing shot which will penetrate a thickness of steel equivalent to over 37 inches of wrought iron. The points of the shot remain intact, although the striking velocities are nearly 2800 feet a second. There are wires which will sustain a load of 170 tons per square inch without fracture. Hadfield, whose labours will, I trust, be continued far into the twentieth century, has given us manganese-steel that will not soften by annealing; while Guillaume has studied the properties of certain nickel-steels that will not expand by heat, and others that contract when heated and expand when cooled,

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Nickel, chromium, titanium, and tungsten are freely used alloyed with iron, and the use of vanadium, uranium, molybdenum, and even glucinium, is suggested. There are steel rails which will remain in use seventeen years, and only lose 5 lbs. per yard, though fifty and a half million tons of traffic have passed over them.

Huge ingots are placed in soaking pits and forged direct by 120-ton hammers, or pressed into shape by 14,000-ton presses. With such machinery the name of our late Member of Council, Benjamin Walker, will always be connected.

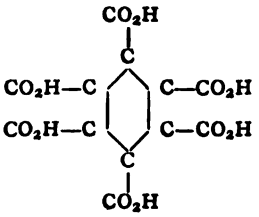
There are steel castings for parts of ships that weigh over 35 tons. We electrically rivet and electrically anneal hardened ship-plates that could not otherwise be drilled. Photomicrography, originated by Sorby in 1864, now enables us to study the pathology of steel, and to suggest remedial measures for its treatment. Stead's works in this field is already recognised as classical. Ewing and Rosenhain have, in a beautiful research, recognised quite recently by its aid that the plasticity of a metal is due to "slip" along the cleavage planes of crystals. Osmond also by its aid shows that the entire structure of certain alloys may be changed by heating to so low a temperature as 225° C.

Passing to questions bearing upon molecular activity, we are still confronted with the marvel that a few tenths per cent of carbon is the main factor in determining the properties of steel. We are, therefore, still repeating the question, "How does the carbon act?" which was raised by Bergman at the end of the eighteenth century. Nevertheless, from the molecular point of view, much may be said in answer to the question. The mystery is in fact lessened now, as it is known that the mode of existence of carbon in iron follows the laws of ordinary saline solutions. Our knowledge is, however, of very recent origin, and we owe mainly to the Alloys Research Committee of the Institution of Mechanical Engineers the development of Matthiessen's view that there is absolute parallelism of the solution of salt in water and carbon in iron.

An ice-floe in a Polar sea contains a small percentage of salt; a red-hot ingot of mild steel holds some two-tenths per cent of carbon, but both the carbon and the salt are in the state of *solid* solution. If the ice had been cooled below −18° C., it would entangle a solidified portion of salt water, which was the last part of the mass to remain fluid. So in the steel ingot, when it has cooled to the ordinary temperature, there is a solidified "mother-liquor" of carburised iron. We do not as yet know whether carbon is dissolved in fluid iron as carbon or as a carbide. We do know, however, that the presence of 0·5 per cent of carbon in iron (such an amount as might occur in a steel rail) lowers the melting-point of the iron from 1600° C. to 1530° C. This lowering has enabled a calculation to be made, the result of which shows that the number of atoms in a molecule of carbon in *fluid* iron at this temperature is probably *two*. It can be shown that at a temperature of 800° C. the number of atoms in the molecule of carbon dissolved is *solid* iron is, in all probability, *three*. At lower temperatures the number of atoms is probably more than three. We metallurgists are not accustomed to think in atoms. Let me, therefore, represent such a three-atom molecule thus:—

without assuming how much iron is associated with the carbon. Following Bergman's experimental method, but with the interval of more than a century separating his work from ours, we investigate the action of acids on carburised iron with a view to ascertain the nature of the atomic grouping of the carbon.

In explaining this I may adopt the appended figure. It is most difficult even to attempt to make questions of atomic grouping clear in a paragraph, but the figure will be helpful. To the historian it suggests vivid pages of Italian history, as the six spheres so arranged constitute the arms of the powerful family of Medici. To the chemist it is a precious symbol, and appeals to him as representing the carbon atoms as grouped in the benzene ring. The result of treating carburised iron with various acids is the formation of marsh-gas and more complicated organic compounds, of which propylene, acetylene, ethylene, and naphtha may be mentioned. Does the nature of these products help us to ascertain the number of the atoms in the carbon molecule as it exists in cold steel? I have consulted organic chemists, among whom I would specially mention my colleague, Dr. Wynne, and their evidence is encouraging. The result of the action of powerful oxidising agents on certain forms of carbon is mellitic acid, $C_6(CO_2H)_6$, which is one of the benzene series, and this favours the view that solid carbon contains twelve, or some multiple of twelve, atoms in the molecule. But mellitic acid is graphically represented in the annexed diagram, the carbon atoms being arranged



as the six spheres are in the arms of the Medici. The group CO_2H is tacked on to each carbon sphere. From this it may be argued that the molecule of solid carbon consists of one or more carbon "rings." In cold steel the group of CO_2H may be replaced by the group Fe_3, which is broken off by the action of suitable solvents, leaving free carbon. Hence the six-atom carbon molecule may exist in steel.

My object is merely to show you how far at the end of the century we have advanced in our knowledge of the mode of action of carbon, and I trust it will be evident that the progress is remarkable. We know that even in solid iron the carbon atom must push and thrust with great vigour, for we can measure the "osmotic pressure" the carbon atom exerts, and, as has just been shown, we can even picture the mode of the atomic grouping in the molecule.

I can only just sum up the evidence as to the occurrence of molecular change in iron. To Gore, and to Barrett, we owe the investigation of the nature of a fact which had long been well known to smiths, that iron on cooling from a bright red heat suddenly emits a glow. We now know that as steel cools down there may be at least six points at which molecular change occurs, accompanied by evolution of heat.

In a series of classical papers of which we are justly proud, for many of them have been communicated to this Institute, our member, Osmond, has shown what is the significance of some of these points, and has won an enduring reputation. We measure and record them photographically as readily as if they were barometric variations. It is known that three points occur in the purest elec-tro-

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iron yet prepared. Two points are connected with the magnetic permeability of iron. One point at least is due to the power iron has of dissolving carbon; two points which occur far below a red heat appear to be due to the presence of hydrogen. Moreover, the molecular condition of steel cooled from an intense white heat is not the same as that of steel which has just been melted. To carry further the evidence as to the effect of an intense heat on iron in a vacuum is the task I have in prospect during my Presidency of the Institute. I may, however, express my agreement with Lockyer's view that the evidence afforded by the atmosphere of the stars shows that our terrestrial iron is a very complex form of matter.

We must not lose sight of those relations of carbon and iron which involve physical equilibrium. Even the astonishing associations of iron and carbonic oxide in the volatile gaseous compound with which the distinguished name of Mond is connected, affords a triumph of dynamic chemistry. It is generally supposed that ozone is dissociated at 160° C., but Dewar has devised a beautiful experiment to prove that ozone has two centres of stability, and one of these is near the melting-point of platinum. It seems to be the same with the relation of hydrogen and iron. We have recently learned that iron and hydrogen appear to be completely dissociated at 800° C., and yet the same iron heated to some higher temperature, say 1200° C., will still yield hydrogen.

Let us suppose that Black, Cort, and Bergman were with us again, and had reviewed the present state of our knowledge and the work accomplished in the century. Let us also suppose that they could go to Sheffield and see an armour-plate rolled and finished for service, and then, visiting our Institute, hear the best explanation we could offer of all the incidental phenomena they had witnessed. Which would they consider the more advanced, our practice or our theory? They would probably hesitate to tell us, but would offer warm congratulations on the immediate prospect of the establishment of a National Physical Laboratory, in which investigations as to the properties of iron and steel will be continued.

Economic Considerations.—The relations subsisting between capital and labour are of vast importance to our industry, and it would not be justifiable to omit reference to them. There is, indeed, abundant precedent for the discussion of this subject in the Presidential Addresses of Mr. Windsor Richards and Sir David Dale.

I venture to hope that the next generation will look back with astonishment to the deplorable aspects presented by what is known as the labour question at the close of the nineteenth century. It is only natural that British enterprise should be met by foreign competition, and I will not dwell on the evidence of our shortcomings in adapting ourselves to the requirements of foreign trade afforded by our "shaming Consular Reports." They are serious enough; but as regards the workmen, their demands for increased wages and reduced hours of work, and, what is far more serious, for the right to determine how little shall be done in those hours, entirely ignore the conditions under which other nations are competing with us. The situation last year was even perilous, for twelve unfinished warships bear eloquent testimony "to the great, though fortunately not irretrievable, misfortunes primarily traceable to the recent engineering dispute."

The multiplied strikes of the last few years have deprived the country of the great advantage it formerly possessed, both as regards excellence of work and punctuality of delivery. To take only the last coal strike; the indictment against the men was thus tersely expressed in *The Times:* "The men lost some £3,000,000 in wages; they crippled the coal trade; they stopped the naval manœuvres; they spread misery broadcast in the district; and they played into the hands of the non-associated owners, who realised large profits, of which but a very small portion found its way into the pockets of the workmen." Capital and labour, which ought to be in amicable association, are too often antagonistic. It may be urged that the antagonism is but a struggle, and that the fittest and strongest must survive, and that we are powerless in the presence of the working of a natural law. Formerly some of us might have been disposed to accept this as inevitable. But my late distinguished colleague, Huxley, in the Romanes Lecture delivered by him at Oxford in 1893, recognised that there are two opposing methods at work in the government of the world. These are respectively the *ethical* and the *cosmic*. The practice of that which is ethically best involves a course of conduct which in all respects is opposed to that which leads to success in the cosmic struggle for existence. "In place of ruthless self-assertion, it demands self-restraint; in place of thrusting aside or treading down all competition, it requires that the individual shall not merely respect, but shall help his fellows; its influence is directed not so much to the survival of the fittest, as to the fitting of as many as possible to survive." Thus Huxley, one of the most acute thinkers of the century, has placed sympathy on a scientific basis by suggesting to us that, in the complex problems which the labour question presents, the ethical method must not be lost sight of; no effort to provide for the well-being of the industrial population can be too persistently adopted. Strangely enough in giving advice to workmen at this critical time, when, as the result of labour conflicts, trade has been lost to the country, we can appeal directly to their self-interest, and in this case industrial influences will be more effective than ethical ones. It is, moreover, through economic means and industrial influences that mankind tends to grow together, and it may confidently be anticipated that the workmen's self-interest, if only it can be rightly directed, will effect the changes in the relation between capital and labour which the moral sense of the men has been unable to accomplish. The highest ethical teaching of true leaders like David Dale, "will then find their late echo in the assent of the multitude."

"Within the trade union movement," write Mr. and Mrs. Sidney Webb in their very interesting work on "The Industrial Democracy," "we find the collectivist-minded working-man grounding his regulation of the conditions of employment upon what we have called the doctrine of a living wage." What that wage should be is most difficult to define; but is there an employer who hears me who is not anxious that each of his people should earn a "living wage," or who feels that the conditions of the life of labourers in the Black Country, as pictured by Charles Dickens in the forties, disgraced humanity? How could people who dwelt under such conditions respect themselves?

How can the legitimate self-interests of the workmen be rightly directed? We must hope that the inclusion of the teaching of economic subjects in the scheme of primary education will do much. We must hope that Boards of arbitration and conciliation will have immediate effect, and will find their full fruition with the rising generation, who may be expected to be more firmly disciplined and to have a higher sense of duty than their fathers. We must trust that frequent discussions between employers and the employed will enable mutual interests to be clearly seen. We must learn that the warmest sympathy with the workmen's rights is not inconsistent, in face of common dangers, with stern and vigorous treatment of labour difficulties which threaten the national prosperity.

Let us hope that advantage will be taken of the prevailing prosperity to place these questions on a satisfactory basis.

Conclusion.—It will have been evident how great a share our country has had in forming the age of steel. The range of properties steel possesses is wide, and by its use the efforts of a multitude of workers have been, as it were, concentrated in a few great efforts which have exerted vast influence on the progress of humanity. Men with most varied aims have, by the use of steel,

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been enabled to reveal their genius. Especially is this true of the Members of the great Institution of Civil Engineers, whose hospitality is so generously extended to us. The forces of Nature have been utilised through the intervention of machinery, which could not have been constructed if steel had not been known. By the adoption of steel distance has been abridged, and it has been possible to express our national attributes of courage and endurance in concrete forms. You who produce steel have enabled the designer of the greatest fleet ever seen to claim that our nation has "become the ship-builders of the world."

As a plastic material steel has served as a vehicle for embodying the imagination of the Art Worker. To the Chemist and Physicist steel presents complex problems for research, and affords boundless hope that further changes in its composition or treatment will enable new wonders to be wrought which will make the future a rich inheritance.

At the end of the century we are hoping that a Royal Charter will be granted to our Institute, the members of which have, as I have shown, done so much. That the well-being of the nation depends on its scientific and industrial progress was recognised in the charter given to that centre of all scientific advance, the Royal Society, in 1662, by His Majesty King Charles II. In this charter the King said: "We have long and fully resolved with Ourself to extend not only the boundaries of the Empire, but also the very arts and sciences." The method by which this was to be effected had been suggested long before by the better-known words of another monarch, who wrote the proverb: "It is the glory of God to conceal a thing, but the honour of kings is to search out a matter." Industrial or scientific truths are hidden, but we have freedom of search by "actual experiment." The humblest investigators of the properties of iron and steel may, therefore, make the resolve of Charles II. and share the glory of Solomon; for, bringing our intellectual gifts into closer union with our practical interests, and broadening the boundaries of the metallurgic art, will assuredly enable us to make better use of our existing possessions, and will lead to the extension of the Empire.

NOTICES OF BOOKS.

New York Experimental Station, Geneva, N.Y. Bulletins No. 150—154. Published by the Station, 1898.

During the past two years the raspberry saw-fly has done serious injury in certain localities in the State. Experiments show that the larvæ can be successfully checked by spraying with hellebore (one ounce to a gallon of water). The grape-vine flea-beetle has also been abundant. Experiments with this insect are not yet complete, but the adults have been checked with Paris green (at the rate of one pound to 50 gallons of water, with the addition of enough slaked lime to make the mixture milky in appearance); this should be applied as a fine spray.

Experiments in ringing grape-vines were begun in 1896 and continued during two seasons. The effect on some varieties was very marked, both the bunches and the berries being larger, and ripening beginning earlier. There can be little doubt that the effect of ringing is devitalising to the plant, but when judiciously managed need not result disastrously.

The apple tree tent caterpillar and the canker worm are easily destroyed by Paris green, green arsenite, and arsenite of lime. The two latter have the advantage of cheapness, and will remain suspended in water much longer.

Commercial fertilisers for potatoes have also occupied some attention, the work described in *Bull.* No. 154 being the continuation of the tests made in 1897. The new tests included sixty-four ¼-acre plots on four farms, and were planned to ascertain the effect of a full amount of potash as compared with two-thirds as much, one-third, and none at all. The fertiliser without potash was as efficient as those containing it, so the variations in amount showed no influence.

In the Director's report for the year is given a description of the new Biological and Dairy Building. A number of illustrations show clearly its construction and equipment. It is now two years since the Station began the publication of the so-called popular *Bulletins*, and they are now sending out over 32,000 copies, and the number is still growing. A number of tests were made on growing fruit, vegetables, &c., from foreign sources in carefully prepared soils, but the only really promising one in the whole list proved to be one of the cabbages of the flat Dutch type.

CORRESPONDENCE.

NEW CONDENSER.

To the Editor of the Chemical News.

Sir,—We note in your issue of May 12th (vol. lxxix., p. 217) a description of a new condenser by F. W. Aston.

We beg to advise you that we have been making a condenser, patented by Mr. Cecil H. Cribb, for some months (and that we have the sole rights for making these in glass), and we enclose particulars of same.

From these particulars you will see that, in the condenser which Mr. Aston describes, there is no new idea whatever. Mr. Cribb's patent covers the making of these condensers in any shape, therefore the one described in the paper is an infringement.—We are, &c.,

C. E. Müller & Co.

148, High Holborn, London, W.C.,
May 31, 1899.

COMPOSITION OF MANGANESE PYRO-PHOSPHATE.

To the Editor of the Chemical News.

Sir,—It will be of interest to analytical chemists to call attention to an error in the latest English edition of Fresenius's "Quantitative Analysis" (A. Vacher, 1876, vol. i., p. 133), where pyrophosphate of manganese is stated to consist of 2MnO 35·50 and PO_5 71. This should, of course, be 2MnO 71, and PO_5 71, and the percentage of these respectively 50 and 50.

In the German edition, from which this was translated, no figures are given for the composition of this substance,—hence the error no doubt arose from want of care in filling out that omission.—I am, &c.,

F. P. Dunnington.

University of Virginia,
May 12, 1899.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

Note.—All degrees of temperature are Centigrade unless otherwise expressed.

Comptes Rendus Hebdomadaires des Séances, de l'Académie des Sciences. Vol. cxxviii., No. 19, May 8, 1899.

Separation of Traces of Bromine existing in Chlorides.—H. Baubigny.—If a known weight of chloride in the form of a saturated or nearly saturated solution, and very rich in copper sulphate, is treated with perman-

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ganate (about one-tenth of the weight of the chloride) in the cold, the whole of the bromine, which the chloride contains in the form of bromide, can be extracted, but at the same time traces of chlorine are also liberated. After this operation, it is sufficient to treat the alkaline liquid from the condenser, where the chlorine and bromine have been collected, at 100° by the ordinary method for chlorine. The liquid contains only minute traces of chlorine, but these can be accurately determined and subtracted from the total result after the first operation.

Impurities of Aluminium.—Adolphe Minet.—The impurities of aluminium prepared by the new electrolytic method consist principally of silicon, iron, and traces of carbon. The exact amounts have been determined for aluminium prepared at different times.

	1890. Per cent.	1893. Per cent.	1897. Per cent.
Silicon	0·90	0·25	0·02
Iron..	0·40	0·40	0·12
Aluminium ..	98 70	99·35	99·86

Phosphide of Magnesium.—Henri Gautier.—The direct combination of magnesium and phosphorus furnishes a phosphide having the formula Mg_3P_2. This compound is decomposed by water very easily, giving magnesium and pure gaseous phosphoretted hydrogen. Its chemical activity is very great; it acts easily on oxygen, chlorine, &c.

The Flame of Hydrogen.—MM. Schlagdenhauffen and Pagel.—Authors generally agree in saying that the hydrogen flame is very pale; but it has been little noticed that the flame is green or blue, according to the purity of the gas. The authors have experimented on this subject, and have arrived at the following conclusions:—(1) The flame of hydrogen, whether pure or impure, becomes decidedly violet-blue when it is pressed down by a cold body, glass or porcelain, with various experimental conditions. (2) This coloration is due, not to the presence of sulphuretted hydrogen, as Salet believed, but to that of seleniuretted hydrogen.

Hydrogenation of Acetylene in presence of Nickel.—Paul Sabatier and J. B. Senderens.—It has already been noticed that nickel in the form of oxide reacts at a low temperature (30° to 45°) on a mixture of equal volumes of ethylene and hydrogen; at 300° it acts on ethylene alone. These results led the authors to investigate the action of hydrogen on acetylene in presence of nickel oxide. They found that nickel serves to produce easily the hydrogenation of acetylene; indeed, that this reaction is produced immediately at a low temperature. It is found that the normal reaction of nickel on acetylene mixed with excess of hydrogen produces ethane, with a slight proportion of ethylene.

Berichte der Deutschen Chemischen Gesellschaft.
Vol. xxxi., July 25, 1898.

On the Racemics.—F. W. Kuster.—The author has endeavoured to prove that the racemics are stable, not only in the crystalline state, but also in solution. He is of opinion that a combination is effected in the liquid mass.

The Nitroso-derivatives of the Fatty Series (Nitroso-isobutyric and Nitro-isobutyric Nitrites).—O. Piloty.—If the nitrite of amidoxyl-isobutyric acid is treated with an oxidising agent in cold aqueous solution, it is transformed into the corresponding nitroso-derivative, $(CH_3)_2.C\begin{matrix}NO\\CN\end{matrix}$; a white crystalline mass fusible at 53°, forming a deep blue liquid, soluble in alcohol, insoluble in water. This nitroso-derivative decomposes with violence at about 80°. If the action of the oxidising agent is prolonged until the decoloration is complete, we obtain the nitro-derivative, $(CH_3)_2.C\begin{matrix}NO_2\\CN\end{matrix}$, in white prisms, fusible at 35°, soluble in all the organic solvents with the exception of ligroïn, and slightly soluble in water.

The Oxysulphonic Acids and the Sultones.—W. Markwald and H. H. Franne.—The authors have obtained a chlorised product from the action of pentachloride of phosphorus on *o*-benzaldehyde-sulphonic acid, and they propose for it the name *tolyl-sultone*. They have also examined an isomer which they call *benzyl-sultone*. The analogy existing between the chemical properties of the ortho-substituted benzylic derivatives and the corresponding "peri" derivatives of naphthalene lead the authors to believe that *o*-dinitrobenzylsulphonic acid ought, by analogy with peridinitronaphthalene sulphonic acid, to give benzylsultone, $C_6H_4\begin{matrix}CH_2\\O\end{matrix}>SO_2$. Experiment has shown this view to be correct.

Synthesis of Phenanthrene and the Hydrogen Derivatives of Phenanthrene by means of α-Naphthoic Acid.—P. Rabe.—When an alcoholic solution of one molecule of acetacetic-sodium ether and one molecule of the ether of Δ'-dihydro-α-naphthoic acid is boiled, the acetacetic ether joins, in the first phase of the reaction, with the double bands of the second ether, giving a δ-ketonic ether. But under the condensing influence of the ethylate of sodium, a closing of the nucleus takes place with the formation of the ether of 1:3-diceto-octohydrophenanthrenecarbonic acid. This ether, by elimination of the carboxy-ethylic group, easily gives 1:3-diceto-octohydrophenanthrene, a strong monobasic acid which may be regarded as an unsaturated oxy-ketone.

MEETINGS FOR THE WEEK.

THURSDAY, 15th.—Chemical, 8. Ballot for the Election of Fellows. "On the Decomposition of Chlorates, with special reference to the Evolution of Chlorine and Oxygen," by W. H. Sodeau, B.Sc. "The Action of Hydrogen Peroxide on Formaldehyde," by A. Harden, M.Sc., Ph.D. "Homocamphoronic and Camphononic Acids," by A. Lapworth and E. M. Chapman. "Action of Silver Compounds on α-Dibromocamphor," by A. Lapworth. "The Colouring-matter of Cotton Flowers," by A. G. Perkin. "Experiments on the Synthesis of Camphoric Acid," by H. A. Auden, W. H. Perkin, jun., and J. L. Rose. "Methylisoamylsuccinic Acid" (Part I.), by W. T. Lawrence.

INSTRUCTION IN
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Manuals: E. Chr. Hansen, "Practical Studies in Fermentation," London (Spon), 1896). Alfred Jörgensen, "Micro-Organisms and Fermentation," London (F. W. Lyon), 1893.

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Further particulars on application to the Director—

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THE CHEMICAL NEWS.

Vol. LXXIX., No. 2064.

A CONTRIBUTION TO THE STUDY OF INVERTINE.

By W. A. OSBORNE, M.B.

That yeast contains a substance acting hydrolytically upon cane-sugar was first discovered by Baudrimont and Dubrunfaut (*Journ. f. Prakt. Chemie*, xiv., 334). Liebig (*Ann. Chem. Pharm.*, cliii., p. 1) pointed out that this constituent of the yeast could be precipitated from a watery extract by basic acetate of lead. Hoppe-Seyler (*Ber. d. Deutsch. Chem. Gesell.*, iv., 810), though, was the first to make any serious attempt to isolate this ferment. Yeast was rubbed up in a mortar with ether, and then an aqueous extract made which possessed invertive properties. Berthelot (*Comptes Rendus*, vol. l., p. 980) made a watery extract of yeast from which the ferment was precipitated by alcohol. Gunning (*Ber. d. Deutsch. Chem. Gesell.*, v., 821) extracted yeast with glycerin, and used alcohol as a precipitant. Donath (*Ber. d. Deutsch. Chem. Gesell.*, viii., 795) first gave the name invertine to this enzyme. Adopting the method of Zulkowski and König, he treated the yeast first with alcohol, filtered off the alcohol and allowed to dry. A watery extract was then made of the yeast, which when shaken with ether gave a gelatinous mass. This latter, when allowed to drop into excess of alcohol, gave a white flocculent precipitate of invertine.

Barth (*Ber. d. Deutsch. Chem. Gesell.*, 1878, p. 118) devised a method of preparing invertine which still continues in use. Yeast was allowed to dry thoroughly at a temperature below 40° C.; it was then subjected to a temperature of 100—105° C. for several hours. A watery extract was then made which, when dropped into excess of alcohol, gave a rich precipitate of the ferment.

The first object of the present research was to select or devise a method of preparing a crude invertine which should have its enzymotic qualities as strong as possible, and which might serve as a basis for further research. For this purpose the following preparations were made:—

A. Half a kilo. of yeast was rubbed up with 500 c.c. 96 per cent alcohol and allowed to stand over night. The alcohol was then filtered off and the residue spread out on a filter-paper and allowed to dry in sunlight. When dry and brittle, it was rubbed up with 300 c.c. chloroform water (5 in 1000) and allowed to stand six days at a temperature of 35° C. At the end of this time the mixture was filtered, and the filtrate dropped into tall cylindrical vessels three-quarters full of 96 per cent alcohol. The precipitate formed was collected, washed once with absolute alcohol, and dried over H_2SO_4 *in vacuo*.

B. In this case the ferment was prepared in the same way as A, with this exception—that the yeast was extracted with water without any previous treatment with alcohol.

C. This invertine was prepared after the recipe of Barth. The extraction was made with chloroform water and lasted six days.

D. As with C, only that in this case the yeast was dehydrated with alcohol before being subjected to the high temperature.

To test the invertive powers of these preparations, an estimation was first made of the percentage amount of soluble matter in each. A solution was then made of each in water containing 2 per cent of soluble matter. Two c.c. of this solution were added in each case to 20 c.c. of a 1 per cent cane-sugar solution in a test-tube, which was then placed in a water-bath at a temperature of 35° C. At the end of half an hour the mixture was boiled and then transferred to a burette. The amount of invert sugar was tested in the usual way by Fehling's solution, using 5 c.c. of the latter.

The accompanying table gives a comparison of results, each being the average of six experiments. It will be seen from this table that invertine A possesses a high degree of solubility, whilst its invertive properties are strong and constant. It was therefore chosen as a starting-point for further research—Invertine I.

A solution of Invertine I. does not coagulate on boiling, and gives no precipitate on saturation with metallic salts or ammonium sulphate, nor on addition of mercuric chloride or ferrocyanide of potassium with acetic acid.* Proteid impurity may therefore be considered absent. The principal impurities are inorganic in nature, amounting sometimes to nearly 50 per cent of the whole. To remove these, Barth had no other method to propose than to dissolve the ferment in water and precipitate with alcohol, and to repeat this process indefinitely. He confessed, however, that the invertine lost more and more of its active properties when subjected to this treatment, and we are thus confronted with the paradox that the purer the ferment is, the weaker it acts. To explain this loss of invertive power, it has been suggested, on the one hand, that alcohol acts injuriously; and, on the other, that the inorganic ingredients belong to the actual molecule of the ferment. It will be seen from the following researches that the greater part of this inorganic matter may be removed without in any way reducing the active properties of the invertine.

A preliminary clue to the nature of these inorganic impurities may be obtained by a consideration of the constitution of the ash left behind on calcining yeast. According to Belohoubek (quoted in "Die Hefe," by Dr. Edmond Kayser, German edition, 1898), this ash contains—

	Per cent.
Phosphoric acid	51·1
Sulphuric acid	0·57
Silicon dioxide	1·60
Chlorine	0·03
Potassium	38·68
Sodium	1·82
Magnesium	4·16
Calcium	1·99
Other substances	0·06

* Zinc sulphate gives a precipitate of phosphates, but this does not occur if the solution be previously acidified.

Invertine.	Yeast.	Invertine obtained. Grms.	Solubility in water.	Starch solution.	Invertine solution.	Time and temperature.	Amount of Inverted solution necessary to reduce 5 c.c. Fehling.
A	Kilo.	5·7	96 per cent	20 c.c. of a 1 per cent solution.	2 c.c. of a 1 per cent solution.	Half hour at 35° C.	3—3½ c.c.
B	Kilo.	17	About 75 per cent.	20 c.c. of a 1 per cent solution.	2 c.c. of a 1 per cent solution.	Half hour at 35° C.	3 c.c.
C	Kilo.	6—8	95—96	20 c.c. of a 1 per cent solution.	2 c.c. of a 1 per cent solution.	Half hour at 35° C.	5—9 c.c.
D	Kilo.	6—8	97	20 c.c. of a 1 per cent solution.	2 c.c. of a 1 per cent solution.	Half hour at 35° C.	∞ (inert).

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Magnesium and potassium phosphate are therefore amongst the most likely components of the mineral element in invertine.

The insoluble residue left behind on dissolving invertine proved to consist chiefly of magnesium phosphate with a slight amount of iron and a certain admixture of organic matter.

If now to the filtrate ammonia be added a fairly heavy precipitate of NH_4MgPO_4 falls.* Being crystalline this precipitate does not enclose any of the ferment in its substance, as is the rule with phosphatic precipitates in general. The filtrate from this precipitate may now be placed *in vacuo* over H_2SO_4, in order to remove NH_3 and water. The ferment so obtained is a brown, resinous, and somewhat hygroscopic mass, readily soluble in water, and possessing strong invertine powers = Invertine II. Ammonia, even in strong excess, seems to exert no injurious action on invertine. To test the comparative strengths of I. and II., 1 c.c. of a 1 per cent solution of each was added to 20 c.c. of a 1 per cent cane-sugar solution, and placed in a water-bath at 35° C. for five minutes. At the end of this time the mixture was boiled and placed in a burette. An estimation was then made of the amount necessary to reduce 5 c.c. Fehling.

I. = 12 c.c.
II. = 11½ ,,

It thus appears that II. is actually stronger than I., which is explained by the fact that in the former there is a higher percentage of actual ferment. It might further be mentioned in this connection, that a strong solution of Invertine II. possessed invertine powers as strong as those just given after lying some years under a bell jar, containing also a small vessel half-full of H_2SO_4, all traces of NH_3 having disappeared.

The proportion of the magnesic phosphate to the remaining mineral impurity may be judged by the two following ash analyses:—

	1.	2.
Invertine I.	44·58	31·62
,, II.	29·3	19·96

About a third, therefore, of the total inorganic impurity is removed by the simple process of treating with NH_3.

As a further step in the process of preparing a pure ferment, a substance was sought for which could form with the invertine an insoluble combination from which the ferment might afterwards be separated.

Potassio-mercuric iodide, which, according to Wroblewski (*Zeitsch. f. Physiol. Chemie*, xxiv., 173), acts so well with diastase, gives no precipitate with invertine. On the other hand, phospho-tungstic acid, in presence of a mineral acid, is a true precipitant. To determine beforehand to what degree mineral acids are injurious to the invertine, the following experiments were made:—

A number of test-tubes were taken, each containing 10 c.c. of a 1 per cent solution of II. To each was added 10 c.c. of dilute acid in varying strengths. The test-tubes were placed in a water-bath at 35° C., and kept there over night. On the following morning the contents of each were neutralised by the corresponding amounts of normal sodium hydrate solution; a few c.c. of cane-sugar solution were added, and the test-tubes placed again in the water-bath for half-an-hour, at the end of which time invert-sugar was tested for by Fehling.

	Strength of acid in a 0·5 solution of II.	Invertine power.
(*a*). HCl ..	1/24 normal	Completely destroyed.
	1/36 ,,	Almost completely destroyed.
	1/40 ,,	Slightly lessened.
	1/48 ,,	Not appreciably lessened.
(*b*). H_2SO_4	1/20 normal	Completely destroyed.
	1/24 ,,	Almost completely destroyed.
	1/36 ,,	Very slightly or not at all lessened.

* Any commercial invertine will give this precipitate with NH_3.

Seeing how readily the invertine is affected by mineral acids, the prospect of success with the phospho-tungstic method is not very great. An attempt, however, to use this method was made, dilute H_2SO_4 being added drop by drop along with the phospho-tungstic solution, whilst the mixture was vigorously stirred. The precipitate was washed with dilute H_2SO_4, treated with $Ba(OH)_2$ and CO_2, but no active ferment could be obtained. Most probably the phospho-tungstic acid is itself injurious to the invertine.

In the next experiments neutral lead acetate was employed. It was found, in preliminary experiments, that to obtain an active ferment the phosphates must first be removed from II. For this purpose either $Ba(NO_3)_2$, with a little NH_3, was added to the solution, or, as the barium phosphate brings down a quantity of ferment, $Mg(NO_3)_2$ and NH_3.

To the filtrate neutral lead acetate solution,* with a little NH_3 was added until no more precipitate formed. The whole was then filtered, and the precipitate washed thoroughly until the wash water was free from nitrates, as proved by the diphenylamine test. The precipitate was then suspended in water, and a stream of H_2S passed through until the colour was uniformly black. The mixture was then filtered, and the filtrate allowed to evaporate at a temperature of 35° C. in a strong current of air.

The great difficulty with this method was to prevent lead sulphide appearing in the final filtrate; acid, as we have seen, could not be added at any stage of the process. In one of the most successful attempts with this method, a clear glassy substance was obtained, faint brown in colour, strongly invertive in property, and containing 4·54 per cent ash.

As the difficulties connected with the semi-solubility of PbS were too great to overcome completely, it was decided to discard this method for the time being, and to try the effect of prolonged dialysis. Accordingly a solution of II. was made, and dialysed for several weeks in an apparatus slightly modified from that described by Wroblewska (*Zeits. f. Phys. Chem.*, xxiv., 173), chloroform being constantly added to the water. Though the dialysing tubes were carefully tested, it was found that the water in the dialysor possessed invertive powers, a small quantity of the ferment having evidently penetrated through the parchment-paper. The contents of the tube were finally taken out, filtered, if necessary, from any slight sediment which had formed, and evaporated in a strong current of air at a temperature of 35° C. = Invertine III.

In every case the substance thus obtained was strongly invertine, and contained inorganic impurity to a comparatively slight degree, as proved by the following ash analyses:—

	1.	2.	3.	4.
Ash analysis ..	1·83	2·24	1·72	1·61 per cent

As, however, dialysis carried out in this manner is a rather tedious process, some improvements were made in order to shorten and facilitate the method. In the first place, phosphates were removed by adding to the solution of II. a slight excess of ordinary laboratory magnesian mixture. The filtrate from this was then dialysed. By means of a double crank arrangement, worked by a small water motor, an alternating up-and-down movement was given to both ends of the parchment tube. By this means both invertine solution and the surrounding water were kept in a continual state of motion. Chloroform was added to both water and solution. When, on testing a small portion of the solution no precipitate was obtained with either $AgNO_3$ or $BaCl_2$, the contents of the tube were taken out, filtered by means of a Pukall filter, and evaporated by boiling *in vacuo*. The temperature remained below 30° C. throughout this latter process, so that the ferment was not in any way injured. When a syrupy consistence had been reached, the ferment was

* I could never succeed in preparing an active ferment by using the basic solution.

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precipitated by addition of excess of alcohol and ether. It was then washed with absolute alcohol and dried *in vacuo* = Invertine IV. Thus prepared, invertine is an extremely light powder, of whitish-grey colour, readily soluble in water, and possessing invertive powers of a high order. As regards inorganic matter, the least obtained on ash analysis was 1·83 per cent.

Constitution of Invertine.

That the large percentage of inorganic matter in ordinary invertine is not a necessary component of the ferment may be deduced from the foregoing facts, namely, that these inorganic constituents may be reduced 90 per cent without making any appreciable diminution of the invertive power.

As regards the classification of invertine amongst organic substances, and specially as regards its relation to albuminous bodies, the following reactions with proteid tests may first be given:—

A. Precipitation tests.
1. Coagulation by boiling = negative.
2. Mineral acids, including metaphosphoric = negative.
3. Metallic salts. *a*. Copper sulphate = positive (faint). *b*. Lead acetate = positive. *c*. Mercuric chloride = negative.
4. Acetic acid and ferro- or ferricyanide of potassium = negative.
5. Saturation with neutral salts, Na_2SO_4, &c., after acidulation = negative.
6. Saturation with ammonium sulphate = negative.
7. Alcohol = positive.
8. Mineral acid and phospho-tungstic or phospho-molybdic acid = positive.
9. Acetic and tannic acids = negative.
10. Potassio-mercuric iodide with HCl (or potassio-bismuth iodide) = negative.
11. Acetic and picric acids = negative.
12. Trichloracetic acid = negative.

B. Colour reactions.
1. Millon's reagent = faint.
2. Xanthoprotein = positive.
3. Adamkiewicz = negative.
4. Buiret = faint.
5. Liebermann's reaction = negative.
6. H_2SO_4 and sugar = negative.

From these reactions it will at once be seen that invertine cannot be classified amongst the ordinary proteids; the possibility, too, of its being allied to peptone, with which it has certain physical properties in common, must also be excluded.

The question may be raised whether the invertine thus prepared is not an admixture of a small amount of active ferment with a relatively large quantity of carbohydrate. To this the answer may be given that its extreme solubility excludes a great many of the carbohydrates; further, that though it indeed gives the Molisch reaction, it does not reduce Fehling; and glycogen, the most likely carbohydrate impurity to be present, is proved absent by the iodine test. The best proof, though, that invertine may be isolated in a comparatively pure condition, is furnished by analysis.

Donath obtained the following percentage composition of invertine:—

C = 40·48 per cent	40·53 per cent
H = 6·88 ,,	6·38 ,,
N = 9·47 ,,	9·36 ,,

Barth obtained the following:—

C = 44·20 per cent	44·60 per cent
H = 8·50 ,,	8·30 ,,
N = 6·40 ,,	5·50 ,,
S = 0·63 ,,	—

These results certainly do not correspond well with each other—a sure proof that the ferment in one or both cases was mixed with some other substance.

The following are the analyses obtained in the present research. In all cases the substance was dried in a toluol bath in an atmosphere of hydrogen. A special ash analysis was also made in most cases.

Invertine III.

	1.	2.	3.	4.
Ash	1·83	2·24	1·72	8·22
*C..	45·1	44·3	44·86	45·07
H	6·69	6·5	6·56	6·46

Invertine IV.

	1.	2.	3.
Ash	5·5	5·17	6·78
C	44·05	44·81	—
H	6·54	6·31	—
N	6·03	5·7	6·58

Invertine prepared by Lead Acetate Method.

	1.	2.	3.	4.
Ash..	8·16	10·59	4·54	11·63
C	42·42	42·13	43·89	44·28
H	6·55	6·55	7·45	6·95

As regards the lead acetate method it was found that in the first two cases the lead present in the invertine had formed with the other ash constituents a glassy substance which enclosed a few particles of charred invertine. The hydrogen values may be taken, though, as correct. In the latter two cases the combustion with oxygen stream was continued for a much longer time. This will possibly account for the high values of H, but C may be taken as approximately correct, as the ash was clear and devoid of carbon particles.

The following may be regarded, therefore, as the average percentage composition of invertine:—

C	44·54
H	6·52
N	6·1

That the values for C and H should remain constant, notwithstanding the different methods of preparation, shows that the invertine was present in a state comparatively pure.

The low percentage of carbon places invertine altogether apart from the proteids.

On the other hand, a distinct similarity may be observed between the percentage composition of invertine and that of chitin, taking Schmiedeberg's formula for the latter (*Arch. für Exper. Pathol. u. Pharm.* xxviii., 41):—

Chitin, $C_{18}H_{30}N_2O_2$ =	C = 46·35
	H = 6·44
	N = 6·01

It is therefore possible that invertine belongs to a class of bodies resembling chitin in chemical structure, amongst which Fraenckel's albamin (*Wiener Sitzungsberichte*, cvii., Abt. II.*b*, p. 819) might also be classified.

Chitin when boiled with HCl gives, as Ledderhose (*Zeit. f. Phys. Chem.*, vols. ii. and iv.) discovered, acetic acid and glucosamine chloride. Experiments made with Invertine IV. showed that HCl, strong or slightly dilute, gives a reducing substance after a few minutes boiling. If the hydrochloric acid be now removed with silver oxide, the solution remains strongly acid, pointing to the probability that some other acid has also been formed. Boiling with HCl produces, if long continued, a black carbon deposit.

This reducing solution, when treated with phenylhydrazine and acetic acid gave, after half an hour in the water-bath, a mass of yellow crystals in rosettes and

* In all these analyses C and H are of course reckoned for the ash-free substance.

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sheaves, which, when washed with acetone and re-crystallised in dilute alcohol, had a melting-point of 198° C. (phenylglucosazone 205° C.) and contained 15·5 per cent nitrogen (phenylglucosazone 15·6 per cent).

Unfortunately the amount of Invertine IV. at disposal was not sufficient to make any thorough investigation of this reducing substance. The author soon hopes, however, to complete this part of the research.

The above research was made in the Physiologisch-chemisches Institut in Tübingen, under the guidance of Professor Hüfner, to whom the author is very especially indebted, not only for the suggestion of the research and advice in carrying it out, but also for a large amount of material which was generously placed at his disposal.

NOTES ON THE ELECTRO-DEPOSITION OF PALLADIUM.*

By SHERARD COWPER-COLES, M.Inst.M.M.

Palladium is usually found associated with platinum, and as a rule it does not exceed 1 per cent. It is generally separated from platinum by chemical processes.

At the present time the uses for palladium are very limited, the demand being considerably less than the supply, consequently the price is low as compared with some other rare metals. The present price is about double that of platinum, but its specific gravity is about half. Its colour is almost as white as that of silver, and it takes a beautiful polish. Palladium is very malleable and ductile, and is harder than platinum. The following table gives the hardness of electro-deposited palladium as compared to other metals:—

Nickel electro-deposited	10·0
Sheffield plate	10·0
Antimony electro-deposited	9·0
Palladium deposited bright..	8·0
Cadmium deposited bright	4·5
Silver electro-deposited and burnished	4·0

The figures give the hardness as represented by the number of grms. weight on a diamond point required to produce a scratch.

Palladium fuses at a somewhat higher temperature than platinum. Moissan has found that palladium, like platinum, dissolves carbon at the temperature of the electric furnace, but does not unite with it, the whole of the carbon separating out as graphite on cooling.

The author has recently used palladium as a protective coating and reflecting surface for parabolic reflectors, some specimens of which are on the table, the whole of the parabolic reflector being made by electro-deposition. The palladium can be deposited quite bright on the surface of the mirror, so that it does not need polishing, which would destroy the true parabolic curve. A deposit of 70 to 80 grains per superficial foot is found to afford a good protective coating. Such a film of palladium is probably transparent, in which case a considerable portion of light would be reflected from the silver surface beneath the protective film of palladium.

Palladium is unchanged by air at ordinary temperatures, but at a moderately high temperature a thin film of oxide is formed which has a bluish colour. At a higher temperature the oxide is decomposed. Palladium alloyed with one-tenth silver is sometimes employed for the graduated scales of astronomical instruments.

Smee devoted some attention to the electro-deposition of palladium, and attempted to deposit metallic palladium from the nitrate, but only succeeded in getting down a black powder. He found ammonio-muriate of palladium dissolved in ammonia to be the best. He also tried iodide of palladium, by adding a solution of iodide of potassium to a solution of palladium, but found it was not a suitable salt for electro-deposition. He also tried palladio-cyanide of potassium. An electrolyte made up of cyanide of potassium is said to take up a considerable quantity of metal and yield the metal freely, so that heavy, reguline deposits can be obtained.

Bertrand has succeeded in obtaining good deposits with a solution formed of the double chloride of palladium and ammonium, made perfectly neutral; a palladium anode was found to dissolve freely.

Gore has electrolysed a solution of chloride of palladium, in which a palladium anode was found to dissolve, and a black deposit of palladium was obtained upon the cathode.

The author has found a solution of palladium ammonium chloride to be one of the best, if not the best, for depositing palladium in a bright form, such as exhibited here to-night. The best proportions are about a 0·62 per cent solution of palladium ammonium chloride dissolved in about a 1 per cent solution of palladium ammonium chloride. The solution is worked at a temperature of about 75° F., the current used per sq. ft. being about 0·12 ampère, the E.M.F. at the terminals of the bath being 4 to 5 volts. The anodes can be either palladium foil or carbon.

* Read before the Institution of Mining and Metallurgy.

THE ESTIMATION OF SULPHUR AND SULPHATE OF COPPER IN ANTIPHYLLOXERIC MIXTURES.

By Dr. G. SCARLATA.

The mixture of sulphur and sulphate of copper, employed now for combatting the diseases of the vine, is the object of numerous falsifications, resulting from speculation and mutual agreement between makers. It is therefore useful to have a simple and rapid method of verifying the composition of these mixtures.

The method now generally in use is quickly performed, but from the point of view of accuracy it leaves much to be desired. It is based on the extraction of the sulphur by sulphide of carbon. Now we know that this extraction may be incomplete if the sample contains the insoluble variety of sulphur.

In the same way, the volumetric titration of the copper does not give absolute certainty, and in analyses done sometimes by inexperienced chemists, the results depend more or less on the particular conditions in which the operator is placed.

I may add that, at the present day, *makers* find means, by suitable additions, to falsify the results of the colorimetric titration of the copper, and prevent the complete extraction of the sulphate of copper by water, except when the water is acidulated.

Having had considerable experience in this class of analysis, I am quite satisfied of the small amount of confidence which should be placed in the methods now used, and I have therefore endeavoured to unite all the conditions necessary for accuracy and rapidity.

My process is based on the two following principles:—

1. The sulphur can be determined by oxidation and titration of the sulphuric acid formed.
2. The sulphate of copper can be determined by the estimation of the sulphuric acid set at liberty by decomposing the sulphate of copper by sulphuretted hydrogen.

The following are the details of manipulation:—Treat 1 grm. of the sample with water acidulated with nitric acid, filter, and wash the residue, which serves for the estimation of the sulphur. This residue is placed in a flask with a round bottom and a long neck, and an excess of fuming nitric acid is added. Heat until the oxidation is complete, pour the liquid into a porcelain crucible, rinse the flask with water, and evaporate the whole on a water-

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bath until the nitric acid is completely eliminated. Take up with cold water, and titrate the sulphuric acid with soda or potash.

To estimate the sulphate of copper, heat 10 grms. of the sample in a crucible placed on a piece of asbestos card, until the sulphur is completely eliminated by volatilisation and combustion. Add sulphuric acid, and heat until white fumes cease coming off. Take up with water and treat the solution with sulphuretted hydrogen, filter off the sulphide of copper, wash with water containing a little sulphuretted hydrogen, collect all the wash waters and boil to drive off the sulphuretted hydrogen, and titrate the sulphuric acid with soda or potash.

I have tested this method with a known mixture containing 3 per cent of sulphate of copper, and obtained the following results:—

Sulphur	96·5 per cent.
Sulphate of copper.. ..	2·9 „

This method, as can be seen, has a degree of accuracy quite sufficient for practical commercial work.

It does not require any special apparatus, and is limited to two titrations of sulphuric acid, which can be effected with the same solution of caustic soda or potash.—*Moniteur Scientifique*, Series 4, xiii. (Part I.), June, 1899.

ON CRYSTALLISED TUNGSTEN.

By L. A. HALLOPEAU.

In a previous paper (*Bull. Soc. Chim.*, Series 3, xix., 997) I have shown that the electrolysis of paratungstate of lithium, by means of platinum electrodes, enables us to obtain crystallised tungsten mixed with a certain quantity of platinum. I have repeated this experiment, slightly prolonging the duration or the electrolysis, and using a current of slightly lower intensity (2·6 ampères and 15 volts; the melted mass was cooled as slowly as possible, then heated successively with water, hydrochloric acid, and lithia, as I have already described. Under these conditions we can obtain needles of tungsten reaching up to 4 m. in length, and which can be isolated in a state of purity by picking them one by one. Their analysis has given me:—Tungsten = 99·64 per cent.

It is in this manner easy to prepare, by the electrolysis of paratungstate of lithium, a small quantity of pure lithium crystallised in very good needles.

These crystals have a grey metallic lustre, like that of steel; they are not magnetic.

When heated to redness in a current of hydrogen, tungsten burns, and is transformed into tungstic acid. This tungstic acid is absolutely pure, and retains the form of the crystals of tungsten.

I have also noted the production of crystallised tungstic acid by the combustion in oxygen of crystallised binoxide of tungsten, the preparation of which I have already described in a previous paper (*Bull. Soc. Chim.*, Series 3, xix., 746).

These facts are analogous to that which is observed whenever tungstic acid is prepared by the calcination of a crystallised tungstate of ammonia; the acid obtained appeared also to be crystallised.

The electrolysis of paratungstate of lithium with iridio-platinum electrodes did not give me good results. As a matter of fact, the oxygen given off at the positive pole forms, with this latter, binoxide of iridium. After treating the product of the electrolysis with water, hydrochloric acid, and lithia, there remain prismatic crystals of a deep blue colour, containing iridium and very rich in tungstic acid. This body thus seems to be a compound of tungstic acid and binoxide of iridium; it is mixed with a small quantity of crystallised tungsten and a little platinum.—*Bull. Soc. Chim.*, Series 3, xxi., No. 6.

THE DETERMINATION OF POTASH AS PERCHLORATE.*

By F. S. SHIVER.

(Concluded from p. 271).

Preparation of Perchloric Acid.

As perchloric acid is not a regular article of commerce, it becomes necessary for each one desiring it to make his own supply. There may be mentioned briefly four methods for its preparation, and the literature in which detailed directions may be found.

The Method as Proposed by Schlæsing.—Prepare first potassium perchlorate from potassium chlorate by heating in the usual way. The mass, after the decomposition of the chlorate is treated with boiling water, and then rapidly cooled; the crystals of potassium perchlorate separate; the potassium chloride remains in solution with some of the perchlorate also. The perchlorate is then dissolved and treated with sufficient quantity of hydrofluosilicic acid to obtain the potassium fluosilicate, the perchloric acid being liberated. After standing a while, the precipitate is filtered off, and the filtered solution containing the perchloric acid is concentrated and treated with ammonia. The ammonia salt is next decomposed by hydrochloric and nitric acids, and the solution then evaporated on a water-bath to a syrupy consistency.

The solution is left in this condition for a day or two, to separate further any crystals of potassium perchlorate it may contain. The supernatant liquid is then ready for use after a blank experiment has been conducted with the same.

Process of Perrey.—Perrey has sought to avoid completely the presence of potash in the reagent. He makes use of the principle recognised first by Sérullas that chloric acid, distilled, furnishes a third of its weight of perchloric acid. Barium chlorate, a salt easily prepared, is dissolved in water, and the solution precipitated with sulphuric acid, leaving the chlorate, however, in slight excess. After filtration, the solution is concentrated and distilled, the distillate being collected for use as soon as white vapours show themselves in the body of the retort.

The product which one receives is contaminated with a little chloric acid and chlorine, which can be expelled on the water-bath. The yield of perchloric acid is about the same as in the Schlœsing process.

For details of these two processes consult Grandeau, "Traité d'Analyse des Matières Agricoles," i., 88—91.

Caspari's Method.—This method is quite similar in principle to the method described by Schlœsing. Potassium chlorate is used as a basis, potassium perchlorate being prepared from it in the usual way. The potassium perchlorate dissolved in water is then treated with hydrofluosilicic acid at the boiling temperature, the reaction being as follows:—

$$2KClO_4 + H_2SiF_6 = K_2SiF_6 + 2HClO_4.$$

The solution is then filtered on an asbestos filter under pressure, the clear filtrate evaporated on a steam-bath to small bulk, and allowed to stand for twenty-four hours, whereby is effected the separation of any remaining potassium fluosilicate or perchlorate. It is again filtered and diluted with an equal quantity of water, and barium chloride added in slight excess to remove last traces of sulphuric acid and hydrofluosilicic acid. The clear supernatant liquid is then poured off and evaporated on a water-bath till white fumes of perchloric acid appear.

The solution is then, after allowing any potassium perchlorate that may be present to separate again, diluted with water, and the excess of barium salt most carefully removed with sulphuric acid. The solution is allowed to stand for several days, then filtered through paper, and is ready for use.

* *Journal of the American Chemical Society*, xxi, No 1.

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For details of the process consult Wiley's "Agricultural Analysis," ii., 290, and *Zeit. Angew. Chem.*, 1898, p. 68.

Kreider's Method.—By far the most simple and rapid of all the methods proposed for the preparation of perchloric acid is that worked out by Kreider. The method depends upon the production of sodium perchlorate from sodium chlorate by heating, in the usual way, the subsequent decomposition of the sodium perchlorate by hydrochloric acid with the liberation of perchloric acid, and the precipitation of sodium chloride, which is separated by decantation or filtration. The filtered solution is concentrated on a water-bath till white fumes of perchloric acid appear, then cooled and diluted with water when it is ready for use.

It is manifest that the acid thus prepared is not chemically pure, since sodium chloride is not absolutely insoluble in hydrochloric acid, but if a portion of the acid prepared as above be tested with silver nitrate it will be readily seen that any sodium chloride which may have remained in solution has been converted into perchlorate. Furthermore, unless the sodium chlorate used contained some potassium, or on evaporation the acid was exposed to fumes of ammonia, the residue from the evaporation of a portion of the acid prepared as above will be entirely soluble in alcohol, and the presence of any sodium perchlorate is therefore entirely unobjectionable.

I have, in the course of my work on this subject, prepared the acid by this method several times, and have always found the process very satisfactory, requiring but little time and attention. In my work, however, I found, as the result of blank determination on the acid thus prepared, a very small residue insoluble in alcohol, for which in all cases corrections were made. This correction was very slight, and in no way condemns the process, since it is a very simple matter to determine it once for all on any lot of acid, and make the proper use of the same in the actual determination.

For detail of the process consult Kreider's article in the *American Journal of Science*, xlix., 445—446.

A CONVENIENT METHOD FOR MAINTAINING REDUCTION OF FERROUS SOLUTIONS.

By WILLIAM S. MYERS.

My reasons for calling attention to this method for maintaining reduction in ferrous solutions are, that it is economical, convenient, and effective, and (so far as I have been able to ascertain) new, in this particular application.

Various methods have been used to keep ferrous solutions reduced, such as the introduction of zinc and sulphuric acid, and the addition of syrups, gums, sulphurous acid, or sulphuric acid. These are either unnecessarily expensive or ineffective, as they may interfere with the uses of pure ferrous solutions, and I have not been able to obtain as satisfactory and permanent results with them as with the method which I have made the subject of this note, namely, the addition of 10 per cent of concentrated sulphuric acid and a suitable amount of iron, in the form of small wrought-iron nails, to a 10 per cent solution of ferrous sulphate. The acid under these conditions liberates hydrogen very slowly, and yet fast enough to nullify the oxidising action of the air, even when the solution is exposed in an open beaker.

I have found that ferrous solutions thus made up will keep for more than a month in a practically unchanged condition, while solutions made up with syrups, gums, or with free acids, and similarly exposed, were very largely ferric at the end of the period, and acidified ferrous ammonium sulphate, $FeSO_4(NH_4)_2SO_4+6H_2O$, was in very little better condition.

When one requires a large amount of ferrous sulphate for qualitative class-room work, for example, an open beaker full of the reagent always in good condition is very useful in saving time, and is of great convenience, and in these respects has been so satisfactory to me that I venture to present the method to the members of the Society.—*Journal of the American Chemical Society*, vol. xxi., No. 1.

PROCEEDINGS OF SOCIETIES.

CHEMICAL SOCIETY.

Ordinary Meeting, June 1st, 1899.

Dr. W. H. Perkin, F.R.S., Vice-President, in the Chair.

Messrs. S. Wellington, P. J. D. Fielding, C. R. Darling, and H. M. Read were formally admitted Fellows of the Society.

Certificates were read for the first time in favour of Messrs. James Dick Dougall, Millom, Cumberland; Ernest Frederick Stephen Lange, Sunny Nook, Victoria Road, Withington, Manchester.

In response to an invitation from the University of Cambridge, the President was delegated by the Council to represent the Society at the Jubilee of Professor Sir G. G. Stokes, and in its name to present the following Address:—

To Sir George Gabriel Stokes, Bart., M.A., D.C.L., LL.D., D.Sc., F.R.S.

We, the undersigned, President and Officers of the Chemical Society, beg, on behalf of the Council and Fellows, to offer you our sincere and hearty felicitations on the occasion of your Jubilee as Lucasian Professor of Mathematics in the University of Cambridge.

The fifty years during which you have held a position so honourable in the ancient University which claims you as among the most distinguished of her sons have witnessed an extraordinary and unprecedented development in those branches of natural knowledge which are immediately connected with the work of your professorship. To this development your own labours as a teacher and an investigator have contributed in no small degree. You have profoundly influenced the teaching of physics wherever this subject is taught, and this influence has of necessity extended into those departments of Chemical Science which are directly dependent upon, or are associated with, physics. We gratefully acknowledge the services you have rendered to chemical physics by your researches on hydrodynamics, by your contributions to the theory and practice of spectrum analysis, and by your optical investigations. Your memorable contribution to our own *Journal*, "On the Application of the Optical Properties of Bodies to the Detection and Discrimination of Organic Substances," made more than a third of a century ago, has borne fruit an hundredfold, and to-day the refractometer and the spectroscope are as indispensable to the chemist as is his balance. We are glad to recognise that your interest in our special field of inquiry, springing from that catholicity which is your characteristic, has in no wise abated, for there is hardly a chemical subject bordering upon those branches of physical research which you have made more especially your own that has not been elucidated and benefited by your kindly criticism and advice. There are many workers in our Society who thankfully acknowledge the ready help which you have rendered to them by your counsel and suggestions.

That you may long continue to enjoy, in health and prosperity, the esteem and respect with which you are universally held by those who labour for the advancement of knowledge and the spread of learning, is the heartfelt

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wish of every member of that body on whose behalf we now address you.

T. E. Thorpe, *President.*
William A. Tilden, *Treasurer.*
Wyndham R. Dunstan, Alexander Scott, } *Secretaries.*
Raphael Meldola, *Foreign Secretary.*

Of the following papers those marked * were read:—

*76. "*The Hydrosulphides, Sulphides, and Polysulphides of Potassium and Sodium.*" By W. Popplewell Bloxam.

In this paper the author shows that there is a very important difference between treating the aqueous solution of a sulphide and one of a hydrosulphide with sulphur. When sulphur is added to aqueous solutions of potassium and sodium sulphides, some thiosulphate is always formed along with the polysulphide, whilst hydrogen sulphide is evolved. This points to the sulphide having become, in part at least, hydrolysed into hydroxide and hydrosulphide. The action of sulphur on aqueous solutions of the pure hydrosulphides gives pure polysulphides with evolution of hydrogen sulphide.

The various wet and dry methods of preparing the sulphides and polysulphides of potassium and sodium described by the many authors who have worked at this subject have been repeated by the author, who concludes that (1) none of these authors could have obtained any polysulphide pure, but only a mixture of polysulphide and thiosulphate; (2) no method exists for separating the polysulphide from the thiosulphate.

The author has succeeded in obtaining the following hydrates of potassium sulphide: $K_2S,2H_2O$; $K_2S,5H_2O$; $K_2S,12H_2O$. These salts can be dehydrated in a current of dry hydrogen, and the potassium sulphide remains stable at 560°. As $K_2S,5H_2O$ loses $5H_2O$, it is evidently not $KHS,KHO,4H_2O$. Sodium sulphide was obtained as $Na_2S,9H_2O$.

By saturation of a solution of potassium hydroxide with hydrogen sulphide, crystals of the composition $2KHS,H_2O$ were obtained, which, like the hydrates of the normal sulphide, could be dehydrated without loss of sulphur. The hydrosulphide was quite stable at 560°.

According to Sabatier, the hydrated crystals of sodium sulphide are easily converted into sodium hydrosulphide by the action of hydrogen sulphide; but the author shows that solutions of sodium sulphide will only take up sufficient hydrogen sulphide to form the hydrosulphide under certain rather restricted conditions as to concentration and temperature. Under favourable conditions, two hydrates were obtained, $NaHS,2H_2O$, $NaHS,3H_2O$, the latter being the stable form.

To prepare the polysulphides, sulphur was dissolved in gently heated solutions of the hydrosulphides, when the following potassium compounds were obtained:— $K_4S_5,10H_2O$, $K_4S_8,6H_2O$, $K_4S_8,19H_2O$, K_4S_9,xH_2O, K_4S_{10},xH_2O, as well as substances approximating in composition to K_4S_6 and K_4S_7.

The only sodium compound obtained in this way was $Na_4S_9,14H_2O$.

*77. "*On the Relative Efficiency of Various Forms of Still-head for Fractional Distillation.*" By Sydney Young, D.Sc., F.R.S.

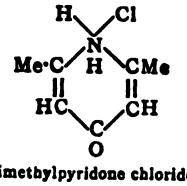
Experiments have been made to test the efficiency of the following forms of still-head, most of which are in general use: (1) plain vertical tubes of different lengths and widths; (2) sloping and spiral tubes; (3) vertical tube with bulbs (Wurtz); (4) the Hempel still-head; (5) the Glinsky dephlegmator; (6) the Le Bel-Henninger dephlegmator. In addition to these a modified Young and Thomas dephlegmator and three new forms of still-head, descriptions of which are given in the paper, have been tested and compared with the others.

As the amount of liquid available for fractionation is often very limited, special attention has been paid to the suitability of the various forms of still-head for the distillation of small as well as of large quantities of liquid. Taking both efficiency and usefulness into account, it is shown that the new forms of still-head are superior to those in general use.

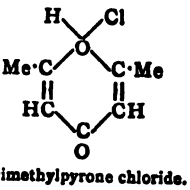
*78. "*The Salts of Dimethylpyrone and the Quadrivalence of Oxygen.*" By J. N. Collie, Ph.D., F.R.S. and Thomas Tickle.

The authors have investigated the series of salts formed by dimethylpyrone with acids. Dimethylpyrone forms, in aqueous solutions with various acids, crystallisable salts. The hydrochloride, hydrobromide, hydriodide, nitrate, oxalate, tartrate, chloracetate, salicylate, picrate, and platinochloride, were prepared; these compounds are produced by direct addition of the acid to the dimethylpyrone without the elimination of water, as in the equation $C_7H_8O_2+HCl=C_7H_8O_2HCl$. On solution in much water, they again break up into dimethylpyrone and the free acid.

Taking into account the molecular structure of dimethylpyrone, the method of preparation, and the properties of these compounds, the authors are inclined to believe that their constitution is similar to that of the salts of nitrogenous and other bases.



Dimethylpyridone chloride.



Dimethylpyrone chloride.

This, however, assumes that oxygen may behave as a quadrivalent element. In favour of this hypothesis, the authors instance such compounds as dimethyl ether hydrochloride, diethyl ether hydriodide, ether peroxide, &c., and they suggest that should compounds similar to the salts they have examined contain nitrogen, phosphorus, sulphur, or iodine, they could be regarded as derived from the hypothetical bases, NH_4OH, PH_4OH, SH_3OH, IH_2OH respectively; hence dimethylpyrone may be looked upon as a derivative of OH_3OH or *oxonium hydrate.*

79. "*The Symmetrical Di-isopropylsuccinic Acids.*" By William A. Bone and C. H. G. Sprankling.

The authors have succeeded in preparing two isomeric symmetrical di-isopropylsuccinic acids, by the action of isopropyl bromide on the sodium derivative of ethyl isopropylcyanosuccinate, and subsequent hydrolysis of the ethereal salt so obtained.

The *trans*-acid, which is quite insoluble in benzene, melts at 226° and has a dissociation constant $k=0{\cdot}0108$. The *cis*-acid, which dissolves in warm benzene, melts at 171—172°, and has a dissociation constant $k=0{\cdot}2255$. Both acids, on treatment with acetyl chloride, give their anhydrides, which are liquid. The anhydrides dissolve in sodium hydrate, forming the sodium salts of the original acids. The anhydride of the *trans*-acid, on being boiled with acetic anhydride for several hours, is converted into the *cis*-anhydride, so that, in this way, the *cis*-acid can be obtained from the *trans*-modification. The behaviour of the new acids with acetyl chloride and acetic anhydride is thus in all respects similar to that of the symmetrical dimethylsuccinic acids. The calcium salts of both acids are sparingly soluble.

Previous workers (Hell and Mayer, *Ber.*, 1889, xxii., 48; Auwers, *Ann.*, 1896, ccxcii., 162) have been able to obtain only the *cis*-acid. Auwers (*loc. cit.*) states that symmetrical di-isopropylsuccinic acid, unlike other symmetrical di-alkylsuccinic acids, exists only in one modification. The authors are also completing an investigation on the symmetrical dipropylsuccinic acids.

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80. "*Active and Inactive Phenylalkyloxyacetic Acids.*" By ALEX. MCKENZIE, M.A., D Sc.

The replacement of the alcoholic hydrogen in active malic, lactic and tartaric acids by alkyl groups causes a striking increase of optical activity. The primary object of the investigation was to ascertain the effect of a similar replacement in the much more highly active mandelic acid.

For the preparation of the active alkylated mandelic acids, the method of alkylation recently applied by Purdie and Pitkeathly (*Trans.*, 1899, lxxv., 157) was adopted. Preliminary experiments with inactive mandelic esters showed that phenylalkyloxyacetic esters were produced. It was found convenient to start with free mandelic acid instead of its esters; thus, by the action of silver oxide and alkyl iodide on *i*-mandelic acid, phenylalkyloxyacetic acids were obtained.

By the interaction of silver oxide, ethyl iodide, and *l*-mandelic acid, a mixture of ethyl *l*-mandelate and *l*-phenylethoxyacetate results. After hydrolysis, *l*-phenylethoxyacetic acid was completely separated from mandelic acid as an oil. Polarimetric observations were made on the acid and on its sodium and barium salts.

l-Phenylmethoxyacetic acid is crystalline, m.p. 63—64°. The sparing solubility of its sodium salt in water afforded a ready method of separating it from mandelic acid. Rotations of the acid in various solvents and of several of its salts in water were made.

From *l*-mandelic acid, phenylpropyloxyacetic acid was obtained as an inactive oil; phenylisopropyloxyacetic acid was crystalline and active.

The molecular rotations of *l*-phenylmethoxyacetic acid and its salts are slightly higher than those of *l*-mandelic acid for equivalent concentrations. The rotations fall on dilution, a minimum being reached with the easily-dissociated salts, but with the acid—which in about 1/50 normal solution is 18 per cent dissociated—the minimum had not been reached. Rimbach's results with *d*-mandelic acid (*Zeit. Physikal. Chem.*, 1899, xxviii., 251) show similar relationships. The rotations for the ethoxy- and isopropyloxy-acids are considerably lower than those of *l*-mandelic acid.

Silver oxide has been used as an alkylating agent with tartrates and lactates without any observations of racemisation in the active products. Although every precaution was taken to avoid racemisation, so far, at least, as this is caused by violent action and rise of temperature, the propyloxy-acid was obtained inactive. Partial racemisation had also taken place in the preparation of ethyl *l*-phenylethoxyacetate by the silver salt method.

81. "*The Chemical Composition of the Oleo-resin of Dacryodes Hexandra.*" By A. MORE.

The oleo-resin consists of essential oil, a resin, and a white crystalline substance, $C_{25}H_{44}O$, melting at 166—167°.

The essential oil contains *lævorotatory pinene* and *lævorotatory sylvestrene*, which is the optical isomer of the sylvestrene described by Atterberg.

The crystalline substance is insoluble in water, and only sparingly soluble in strong alcohol. By the action of acetic anhydride it yields a cryatalline mono-acetate, m. p. 200°, and it therefore appears to be an alcohol. It is unaffected by potash and by all ordinary reagents. A tetranitro-derivative is produced by the action of fuming nitric acid. Chromic acid in acetic acid solution, while oxidising it, appears to cause two molecules to combine; the product is a feeble acid, the molecular weight of which was determined by the cryoscopic method. The substance is probably identical with Personne's ilicic alcohol, m. p. 175°, with which it agrees in composition, and which gives an acetyl derivative melting at 204—206°.

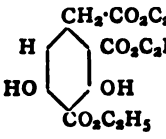
82. "*The Condensation of Ethyl Acetonedicarboxylate: the Constitution of Triethyl Orcintricarboxylate.*" By DAVID SMILES JERDAN.

In the first part of this paper the author discusses the action of condensing agents on ethyl acetonedicarboxylate. Two condensation agents have already been described, namely, a triethyl orcintricarboxylate, $C_{16}H_{20}O_8$ (Cornelius and von Pechmann, *Ber.*, 1886, xix., 1446; von Pechmann and Wolman, *Ber.*, 1898, xxxi., 2014), and a lactone, $C_{12}H_{10}O_7$, which was discovered by the author (*Trans.* 1887, lxxi., 1106), and shown to be a derivative of phloroglucinol. Triethyl orcintricarboxylate was originally obtained by the action of sodium on ethyl acetone dicarboxylate, and afterwards by dissolving the ester in alcohol, saturating the solution with hydrogen chloride, and allowing the mixture to stand some weeks. The lactone, $C_{12}H_{10}O_7$, was first prepared by the action of sodium on ethyl acetone dicarboxylate dissolved in benzene. The author has recently found that both substances are formed by the action of sodium ethylate on an alcoholic solution of ethyl acetone dicarboxylate, and further, that small quantities of a number of metals and of their oxides are capable of bringing about the condensation of relatively large quantities of ethyl acetonedicarboxylate. Thus the ester, when heated with 1/800th part of its weight of sodium, gives a 30 per cent yield of triethyl orcintricarboxylate. The probable course of this reaction is discussed.

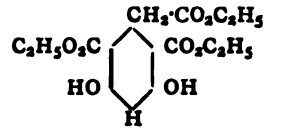
A new condensation product, $C_{14}H_{16}O_8$, which melts at 141°, has been obtained by the action of magnesium on ethyl acetone-dicarboxylate in presence of ethyl chloracetate, and has been shown to be a *diethyl orcintricarboxylate*. It is derived from the same orcintricarboxylic acid as the triethyl ester already mentioned, as is proved by its conversion into the triethyl ester by esterification.

The second part of the paper contains the results of an investigation into the constitution of triethyl orcintricarboxylate. Cornelius and von Pechmann (*loc. cit.*) pointed out that this substance may have one or other of the two formulæ:—

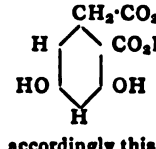
I.

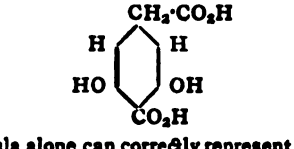


II.



The author has obtained from triethyl orcintricarboxylate, and from the diethyl orcintricarboxylate (m. p. 141°) already mentioned, derivatives of two orcindicarboxylic acids, both of which have been shown to contain the group $-CH_2-COOH$. Only formula I., the asymmetric formula for triethyl orcintricarboxylate, admits of the formation of two such acids, namely:—





and accordingly this formula alone can correctly represent the constitution of triethyl orcintricarboxylate.

83. "*A Series of Substituted Nitrogen Chlorides.*" By F. D. CHATTAWAY and K. J. P. ORTON.

Compounds in which halogen is attached to nitrogen have been little studied, although a number of isolated examples are known. In continuation of our work on nitrogen iodide, we have studied this nitrogen halogen linkage, and have obtained a very large number of compounds in which it occurs.

In this paper the disubstitution products of nitrogen chloride are considered, containing formyl, acetyl, and benzoyl, together with a phenyl or a substituted phenyl residue.

These form a well-defined group of compounds, phenyl acetyl nitrogen chloride discovered by Bender being one of the simplest members.

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They are readily obtained from the corresponding formanilide, acetanilide, or benzanilide by the action of hypochlorous acid under regulated conditions.

$$\frac{RCO}{R'}>NH + HOCl = \frac{RCO}{R'}>NCl + H_2O.$$

The method generally employed is to add gradually the calculated quantity of calcium hypochlorite to the anilide suspended in a saturated solution of potassium bicarbonate.

The substituted nitrogen chlorides are all stable solids of low melting point, crystallising well in large, colourless, transparent plates or prisms. They dissolve readily in chloroform, carbon bisulphide, and benzene, but only sparingly in ligroin.

They react very readily with hydrochloric acid, hydriodic acid, and alkaline hydrogen peroxide, liberating chlorine, iodine, and oxygen respectively, and reforming the anilide. They act with great energy upon aniline, giving chloranilines. The most remarkable change, however, which these compounds undergo takes place when they are heated. When an unsubstituted phenyl-group is attached to the nitrogen, the chlorine and the para-hydrogen atom of the nucleus change places, and a para-chloranilide is formed. With a para-chlorphenyl group attached to the nitrogen, a similar change takes place on heating, the chlorine, however, now going into the ortho-position. Similar changes are brought about when these nitrogen chlorides are warmed with water or dilute acids.

If, however, both the para- and ortho-positions in the phenyl nucleus are occupied, *e.g.*, by chlorine atoms, no intramolecular change ensues, but the molecule breaks down in a somewhat complicated way which apparently depends on the nature of the acid radicle attached to the nitrogen; in the case of the formyl and acetyl derivatives, chlorine is set free; with the benzoyl compound, benzoyl chloride is evolved. Phenyl acetyl nitrogen chloride has been prepared by the bicarbonate method, a theoretical yield being obtained; it crystallises in large, transparent plates.

The following compounds have been prepared:—

Phenylformyl nitrogen chloride, $HCON(C_6H_5)\cdot Cl$, long, transparent prisms. M. p. 47°. *Para-chlor-phenyl formyl nitrogen chloride*, $HCON(C_6H_4Cl)\cdot Cl$, long, transparent prisms. M. p. 95—96°. 2 : 4-*dichlor-phenyl formyl nitrogen chloride*, $HCON(C_6H_3Cl_2)\cdot Cl$, colourless, transparent plates. M. p. 44°. *Para-chlor-phenyl acetyl nitrogen chloride*, $CH_3CON(C_6H_4Cl)\cdot Cl$, colourless plates. M. p. 82°. 2 : 4-*dichlor-phenyl acetyl nitrogen chloride*, $CH_3CON(C_6H_3Cl_2)\cdot Cl$, large, glittering plates. M. p. 68°. *Phenyl benzoyl nitrogen chloride*, $C_6H_5CON(C_6H_5)\cdot Cl$, colourless plates. M. p. 77°. 2 : 4-*dichlor-benzoyl nitrogen chloride*, $C_6H_5CON(C_6H_3Cl_2)\cdot Cl$, large, colourless plates. M. p. 86°.

We believe that the oil obtained by Witt, and regarded by him as a hypochlorous acid addition product of 2 : 4-dichlor-acetanilide, is impure 2 : 4-dichlor-phenyl acetyl nitrogen chloride.

PHYSICAL SOCIETY.

Ordinary Meeting, June 9th, 1899.

Prof. Oliver Lodge, F.R.S., President, in the Chair.

The Secretary read a paper by Mr. C. G. Lamb "*On the Distribution of Magnetic Induction in a Long Iron Bar.*"

A Lowmoor iron rod, whose length was 250 times its diameter, was taken, and a B-H curve plotted by ballistic measurements made with a search coil at the centre of the bar. The search coil was then moved along the bar, and the distribution of induction was determined for magnetising forces varying from H = 0·74 to H = 35·0. Up to fields of 3·35 the induction leaks out more and more quickly as H increases, but above this value the induction tends to keep in more and more. From the curves obtained the mean induction was deduced, as well as the distance of the resultant pole from the middle of the bar. It is shown that this distance first decreases and then increases with the rise in field strength. According to the ellipsoidal theory it should be constant. The bar was then made into a ring, and the B-H curves again determined. From these curves—together with known relations between B, H, and p—curves showing the variation of p along the bar were constructed.

The Chairman gave a general explanation of the way the leakage depended upon the permeability in the case of a long iron bar.

A paper "*On the Absolute Value of the Freezing-point*" was read by Mr. Rose Innes.

The corrected values of the absolute value of the freezing-point, determined by Lord Kelvin from experiments on hydrogen, air, and carbonic acid, contain discrepancies amounting to ½ per cent between the carbonic acid and the hydrogen, while the separate measurements for carbonic acid agree among themselves to about ¼ per cent. Starting with Lord Kelvin's equation for the forcing of a gas through a plug, the author has obtained a formula for the absolute value of the freezing-point, which can be worked out from the experimental researches of Regnault. The formula is based on the experimental proof by Joule and Kelvin, that the ratio between the cooling effect for atmosphere of differential pressure and the pressure is constant for all pressures. Applying data from Regnault's experiments to the formula deduced by the author, the values of the freezing point are practically the same as those given by Lord Kelvin. Hence it is thought probable that the discrepancies are due to inaccuracies in the experiments of Regnault which were conducted at constant pressure. The value of the zero calculated from experiments on hydrogen at constant volume made by M. Chappuis, is, if we treat hydrogen as a perfect gas, 237·034. Applying a thermodynamic correction for the deviation of hydrogen from the laws of a perfect gas, the value of the freezing-point becomes 273·19. This figure agrees very closely with the value 273·14 obtained by Lord Kelvin from the constant pressure experiments on air. The correction has only been applied to hydrogen, because in this case it is so small that a large percentage error in its determination has a very small effect upon the absolute value of the freezing-point. In constant-pressure work the experiments are difficult to carry out, and the correction is easily applied while in constant-volume work, the experiments are easily performed, and the thermodynamic correction is difficult to apply.

Prof. Gray expressed his interest in the manner in which Mr. Rose-Innes had obtained his results without using the experimental data of Joule and Kelvin, and pointed out that Lord Kelvin attached most importance to the results he had obtained for air. It would be useful to have the gas constants re-determined with greater accuracy. The compensating arrangement devised by Prof. Callendar would enable experiments at constant pressure to be carried out satisfactorily.

Dr. Lehfeldt drew attention to the sign of the correction applied by the author, and asked if it should not be negative instead of positive. He pointed out that variation in the specific heat of a gas might affect the formula, and said that Boltzmann had shown that it was impossible to determine an absolute temperature without introducing calorimetric measurements. As Joule and Kelvin had sometimes found positive and sometimes negative values for the cooling effect in the case of hydrogen large percentage errors might occur in the value of the correction.

Mr. Blakesley asked what the probable error was in the numbers given by Lord Kelvin.

Mr. Watson said that the author had calculated the

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value of the freezing-point from experiments on hydrogen, and had shown that the result agreed closely with the value of the zero deduced by Lord Kelvin from experiments on air. He would like to know what agreement would be got by applying Mr. Rose-Innes's correction to the case of air.

Mr. Rose-Innes, in replying, said he agreed with Prof. Gray that it would be useful to have the contents redetermined. It was only in their early work that Joule and Kelvin observed a cooling effect for hydrogen, the bulk of the experiments giving a heating effect. The sign of the correction depended on the increase or decrease of the effect with temperature, and was positive in the case of hydrogen. Regnault has proved experimentally that the value of the specific heat is constant.

NOTICES OF BOOKS.

A History of Physics in its Elementary Branches, including the Evolution of Physical Laboratories. By Florian Cajori. New York and London: Macmillan and Co. 1899. Pp. viii.—322. 8vo. Ill.

Works on the history of the comprehensive subject of physics are not numerous; that by Joh. Christ. Sturmuis, published at Nuremberg in 1676, recorded the notable inventions made in the earlier part of the seventeenth century, and is of antiquarian interest merely. Germany has produced several:—J. C. Fischer's "Geschichte der Physik (1801-1808), extends to eight volumes; August Heller's work with the same title (1882-84), in two volumes; Poggendorff's "Geschichte" (1879), in one volume, and Rosenberger's treatise embodying synchronistic tables (1882-90), in three volumes, are the principal ones in the German language. In the French language we have G. Libri's "Histoire" (1838-41), which, however, is confined to Italy; A. Libe's "Histoire Philosophique" (1810), Max Marie's voluminous work (1883 88), in twelve volumes, and F. Hoefer's condensed sketch in one volume (1872). Authors writing in English seem to have neglected this topic, for if we except Baden Powell's "History of Natural Philosophy" (1842), which moreover omits heat and electricity, and William Whewell's comprehensive "History of the Inductive Sciences" (1837), students will not readily find an English work that covers the field from the earliest period to the present time. This need has now been filled by Dr. Florian Cajori, Professor of Physics in Colorado College. The progress of discovery in mechanics, light, heat, electricity and magnetism, and in sound, is set forth in eight distinct periods, viz., the Greeks, the Romans, the Arabs, the Middle Ages, the Renaissance, the Seventeenth Century, the Eighteenth Century, and the Nineteenth Century. There are also chapters on the Causes of Failure of Greek Physical Inquiry, and on the Inductive Method of Scientific Inquiry, which latter is rather brief and inadequate; numerous references, however, in the footnote enable a student to extend his reading on the subject. These references to authorities are very numerous throughout the work, and form a valuable feature, furnishing proofs of statements as well as means of pursuing the topics in greater detail. The author shows a wide knowledge of the sources of history, not merely of the standard works, but the isolated essays and notes scattered throughout periodicals. This has enabled Professor Cajori to give credit wherever it is due, without national bias.

In the preface the author refers to the necessity of limiting the size of the book and the consequent omission of a few subjects that properly belong to elementary physics; this restriction to 300 pages has caused utmost condensation and prevented the author from elaborating the vast number of topics, giving the work a paragraphic style that does him injustice. We hope that the work may soon go to a second edition, and that author and publisher may see fit to enlarge the volume 50 per cent.

Biographical sketches of those who have contributed to the advancement of physical science occur throughout the book, which is brought down to the current decade.

A concluding chapter deals with the evolution of physical laboratories. The illustrations are few in number and portraits are notably lacking. The index is full. The reviewer knows of no book in the English language that covers the ground so satisfactorily as the one before him.

H. C. B.

Handbook of Public Health, Laboratory Work, and Food Inspection. Part I. By O. W. Andrews, M.B., B.S., M.R.C.S., Surgeon R.N., &c. Portsmouth: Charpentier and Co. Pp. 66.

The volume now before us is the first of three, comprising a series of Lectures delivered by the author to the Surgeons on Entry, Royal Navy.

Vol I. treats of the points to be observed in the inspection of fish, flesh, and fowl, intended for human food, so far as they are dealt with in the course of instruction at the R. N. Hospital, Haslar.

A number of illustrations are given of parasites, &c., injurious to human beings, as well as various fish found in distant parts of the world; a good rule to remember with regard to fish is, that those with scales are wholesome, while those without are not.

Chemical Analysis, Qualitative and Quantitative. By W. Briggs, M.A., LL.B., F.C.S., and R. W. Stewart, D.Sc. (Lond.). The University Tutorial Series. London: W. B. Clive. Pp. 128.

This is a useful book for beginners, and appears to be specially adapted for those students who are unable to attend regular laboratory classes, but have to depend to a great extent on their own resources at home. Instead of only the bare instructions being given for carrying out analytical operations, the reason for each step is explained, and also the action or reaction that takes place; for this reason the book is slightly larger than most books for beginners, a fact which is, however, justified by the result.

Chemical Novelties for 1899. ("Les Nouveautés Chimique pour 1899"). By C. Poulenc. With 196 Figures in the Text. Paris: Baillière et Fils. 1899. Pp. 364.

The latest forms of apparatus used in chemical laboratories are reviewed in this volume. As the science of chemistry advances, so must the apparatus be modified and improved. The brilliant work of M. Moissan, in Paris, and Prof. Dewar, Lord Rayleigh, and Prof. Ramsay, in our own country, necessitate constant improvement and invention in the tools and material of the chemist. In the first chapter descriptions will be found of physical apparatus used particularly in chemistry, among which are G. Müller's compensation thermometer, Schlœsing's apparatus for determining the density of small volumes of gas, picnometers by Fuchs, Landsberg's method for the determination of molecular weights by boiling-points, &c.

In Chapter II. improvements in furnaces, ovens, refrigerators, &c., are described, as well as a new method for the manufacture of acetylene, new mercury pumps, air compressors, &c.

The third Chapter deals with general analysis, special mention being made of Leger's eudiometer and Buisson's apparatus for gas analysis; in metallurgical analysis we find Campredon's method for the estimation of sulphur, and a new microscope by Retjo for the examination of metals.

Chapter IV. deals with electricity, and Chapter V., and last, describes all the latest forms of apparatus employed in the important and growing science of bacteriology.

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CHEMICAL NOTICES FROM FOREIGN SOURCES.

Note.—All degrees of temperature are Centigrade unless otherwise expressed.

Comptes Rendus Hebdomadaires des Séances, de l'Académie des Sciences. Vol. cxxviii., No. 20, May 15, 1899.

A New Preparation and some New Properties of Pentabromide of Tungsten. — Ed. Defacoz. — The action of dry gaseous hydrobromic acid on pure hexachloride of tungsten affords a new method of preparation of tungsten pentabromide. The action takes place at about 250°. The pentabromide thus obtained is well crystalline in needles. It is very hygroscopic and easily decomposes in presence of water, giving the blue oxide. It is soluble in a great number of liquids—carbon tetrachloride, chloroform, bromoform, absolute alcohol, ether, terebene, and benzene—but the solvent must he completely anhydrous. That it has been obtained in a good state of purity is proved by analysis.

Mixed Halogen Salts of Lead.—V. Thomas.—In a recent paper the author showed that chloride and iodide of lead were susceptible of uniting in equal molecular weights to form a well-defined chloriodide. The present paper gives an account of the further study of this and other mixed lead halogen salts. Chlorobromides are formed by the following methods:—(1) Action of hydracids on the halogen salts of lead. (2) Solution of lead chloride in a solution of bromide or *vice versa*. (3) Action of chloride and bromide of an alkali on chloride and bromide of lead. (4) Action of bromine on chloriodides. The last two methods give the best results. The compound formed is anhydrous and crystalline, and can be kept for some months without decomposition; it is soluble in water, but is liable to be decomposed if the solution is very dilute. Bromiodides are produced under analogous conditions to those which produce the chlorobromides.

Separation and Estimation of Traces of Bromine in presence of a large Excess of Chlorine.— H. Baubigny.—In a very recent paper, the author described a method by which minute traces of bromine could be estimated in a large excess of chloride solution, by treating a concentrated solution of the chloride with a mixture of permanganate and copper sulphate. The present paper describes an improved method. Instead of employing the oxidising mixture, a small amount of chlorine is added to the chloride solution—sufficient to displace the bromine. By this method the whole analysis can be completed in four or five hours, and with very great accuracy. It has been possible to recognise and to estimate less than half a milligrm. of bromine in 10 grms. of sea-salt.

Activity of Manganese in Relation to the Phosphorescence of Sulphide of Strontium. — José Rodriguez Mourelo.—M. Lecoq de Boisbaudran has made experiments *in vacuo* on the phosphorescence of mixtures of different substances containing small quantities of sulphate of manganese which in themselves were not phosphorescent when subjected to electric action. The author continues this research by investigating the phosphorescent properties of manganese when mixed with sulphide of strontium without using a vacuum or electric current, and he finds that, in the same manner as the sub-nitrate of bismuth, carbonate of manganese dissolved in a quantity of sulphide of strontium, renders the latter phosphorescent, with a very clear dark green light, after the mixture has been heated to redness for about three hours—the necessary time for the luminous property to develope with the greatest intensity.

Berichte der Deutschen Chemischen Gesellschaft. Vol. xxxi., September 26, 1898.

Partial Racemisation.—A. Ladenburg and G. Doctor.—The authors have attempted to prepare a semi-racemic salt; they tried the neutral racemate of strychnine, which crystallises in warm water in needles fusible at 222°. To prove that this salt is not a mixture, but a well-defined chemical compound, they compared it with the right- and left-handed tartrates, and found that its properties were not those of a mixture; especially, its density is not the mean of the two others, and a mixture of equal parts of the right- and left-handed salts melts at 234°.

Adipic Aldehyde.—A. Baeyer.—Fifty grms. of suberic acid are treated with 100 grms. of tribromide of phosphorus and 180 grms. of bromine for eight to ten hours on a water-bath, the dibromo-suberic acid formed is precipitated with cold water and re-crystallised in boiling water. 30 grms. of this acid are then heated with 60 grms. of crystallised baryta and 90 grms. of water, with a reflux condenser fitted to the flask. The barium salt of dioxysuberic acid which is deposited is decomposed by sulphuric acid, and the dioxysuberic acid is crystallised in boiling water. To effect oxidation, dioxysuberic acid (10 grms.), binoxide of lead (20 grms.), acetic acid (30 grms.), and phosphoric acid at 25 per cent (30 grms.) are heated on the water-bath for four hours. The product is then drawn off by a current of steam. Under these conditions, the adipic acid which is at first formed is immediately transformed either into polymers or into the *cyclopentenemethylal*-1. This aldehyde occurs in the form of a mobile liquid having an odour similar to that of benzaldehyde; it decomposes very rapidly and is easily soluble in water.

Combinations of Chloral with Formic Aldehyde.—A. Pinner.—Formic aldehyde unites very easily with chloral in the presence of concentrated sulphuric acid, giving rise to a sort of oily molecular compound, insoluble in water, completely dissociated on distillation, and partially decomposed by water at the ordinary temperature. If, however, we use a large excess of sulphuric acid, we obtain two crystalline products having the formulæ $(C_5H_3Cl_3O_2)_2$ and $C_5H_4Cl_6O_3$, and a third resinous body. These three bodies behave in the same way as the products of condensation of chloral and the aromatic carbides described by v. Baeyer. The resinous compound has the formula $C_5H_6Cl_6O_4$; boiling alcoholic potash splits it up into oxalic and glycolic acids.

Tautomery of Acetylacetic Ether.—K. Schaum.—A controversial paper, not suitable for abstraction.

On δ-Dimethyl-levulic Acid (Methyl-2-hexanone-3-oïc).—D. Tiemann and F. W. Semmler.—The authors have identified the ω-dimethyl-levulic acid which they obtained by the oxidation of tanacetophorone with the δ-dimethyl-levulic acid described by MM. Fittig and Conrad; it melts at 42—43°. Its oxime,—

$$CH_3.CH.C(NOH).CH_2.CH_2.CO_2H$$
$$\quad\quad\quad

formed into a lead salt, and this latter decomposed by sulphuretted hydrogen. This acid is in the form of a crystalline mass soluble in ether, fusing with decomposition at 186—188°. Aqueous solutions of this acid lose carbonic acid on boiling. To prepare the isomeric dicarbonic acids, the tetracarbonic acid is heated at 160° to tranquil fusion, the residue (40 grms.) is dissolved in warm acetic anhydride (150 grms.), and the product submitted to fractional distillation in vacuo. The portion passing at 215—225° at 90 m.m. is the anhydride of the cis-pentamethylenedicarbonic acid, $C_5H_8(CO)_2O$. The cis acid is partially transformed into the cis-trans by heating it with water or hydrochloric acid in a sealed tube to 180°. The alkaline salts of these two acids are hygroscopic masses extremely soluble in alcohol and water.

Action of Chlorofumaric Ethers on the Amidoximes.—C. Wolf.—When we heat a solution of benzylamidoxime in absolute alcohol with chlorofumaric acid in the presence of ethylate of sodium on a water-bath, we obtain among the products of the reaction a compound possessing acid properties and answering to the formula $C_{13}H_{12}N_2O_4$; it crystallises in long silky needles fusible at 154°; it is not coloured by ferric chloride, and does not fix bromine; its argentic derivative, $C_{13}H_{11}N_2O_4Ag$, melts at 94°. The methylic ether crystallises in flakes fusible at 104° and soluble in dilute alcohol. The corresponding acid is barely soluble in the organic solvents. Phenylethylenamidoxime and chlorofumaric ether unite, giving a compound fusing at 158°.

On Azelaone and Azelaol.—K. Derlon.—The author has studied the products of the dry distillation of azelaate of calcium, looking specially for the octomethylenecetone which should be formed according to the equation—

$$CH_2\begin{matrix}CH_2.CH_2.CH_2.CO_2\\CH_2.CH_2.CH_2.CO_2\end{matrix}>Ca = CaCO_3 + CH_2\begin{matrix}CH_2.CH_2.CH_2\\CH_2.CH_2.CH_2\end{matrix}>CO.$$

An oily layer was first obtained on heating small portions of the salt with its own weight of slaked lime. This product is purified first by a current of steam, then by fractional distillation in vacuo; finally, three portions are isolated, boiling respectively at 45—80°, 80—91°, and 91—105° at 22 m.m. The second fraction answers to the formula $C_8H_{14}O$; it gives a bisulphitic derivative, crystallised in extremely deliquescent small flakes, which could not be purified. The reduction of octomethylenecetone by means of sodium and boiling alcohol gives rise to the formation of the corresponding alcohol, azelaol, a liquid slightly soluble in water, boiling at 187—188° at 746 m.m.

On Methylasparagine.—A. Piutti.—Methylasparagine was obtained by the action of ammonia on citraconic anhydride,—

$$\begin{matrix}CH.CO\\\|\\CH_3.C—CO\end{matrix}>O + 2NH_3 = \begin{matrix}CH_2—CO.NH_2\\|\\CH_3.C(NH_2).CO_2H\end{matrix}.$$

The operation is effected in an autoclave heated to 108—110°. 30 c.c. of the anhydride and 250 c.c. of saturated alcoholic ammonia are used. After six hours the product is evaporated to drive off the ammonia and alcohol, and the methylasparagine is transformed into its cupric derivative in blue clinorhombic plates, soluble in water, having the formula $(C_5H_9N_2O_3)_2Cu.2H_2O$. This salt is then decomposed by a current of sulphuretted hydrogen, and methylasparagine (glutamine) is obtained in the form of efflorescent rhombic tables containing 1 molecule of water; it melts at 254—256°, and is slightly soluble in alcohol; it does not precipitate the salts of silver, lead, or calcium; the salts it forms are very soluble.

Preparation of Phenylhydrazone of Alloxane from Barbituric Acid.—O. Kuhling.—A solution of chloride of diazobenzene is poured gradually into an aqueous solution of barbituric acid and hydrochloric acid. A yellow crystalline precipitate is formed, fusible at 284°, almost insoluble in water, alcohol, and ether.

MISCELLANEOUS.

Royal Institution.—A General Monthly Meeting of the Members of the Royal Institution was held on the 5th instant, His Grace the Duke of Northumberland, K.G., President, presiding. The following were elected members:—Mrs. C. M. Armstrong, Mr. R. Bentley, Sir E. Courtenay Boyle, K.C.B., Mr. R. M. Cowie, Mr. H. H. Cunynghame, Mrs. H. H. Cunynghame, Mr. H. W. Grigg, Mr. O. V. Kilvington, Mr. T. Matthews, Mrs. T. L. Mears, Mr. W. B. Myers-Beswick, Mr. T. C. Owen, Mrs. R. Palmer Thomas, Mrs. Twopeny, Mr. T. Terrell, and the Rev. C. E. Wright. The special thanks of the Members were returned to Mrs. Wigan for her donation of £10 10s., and to Mr. Thomas A. Rogers for his donation of £10 10s. to the fund for the Promotion of Experimental Research at Low Temperatures. The special thanks of the Members were returned to Mr. Hugh Spottiswoode for his valuable gift to the Royal Institution of his father's collection of physical apparatus.

Royal Academy of Science of Turin.—In accordance with the will of the late M. le Sénateur Thomas Vallauri, the Royal Academy of Science of Turin will award a prize to whichever scientific man—either an Italian or of any other nationality—who shall, between January 1, 1899, and December 31, 1902, publish the most important research in the domain of physical science in the widest acceptance of the term. Another prize will also be awarded by the Academy — without distinction of nationality—to the *savant* who, between January 1, 1903, and December 31, 1906, publishes the best critical work on Latin literature. The value of each prize will be 30,000 Italian livres net, less the Italian tax, or about £1000. The prizes will be given one year after being awarded. Members of the Academy, either resident or foreign, will not be eligible to compete. No notice will be taken of manuscript work.

MEETINGS FOR THE WEEK.

WEDNESDAY, 21st.—Microscopical, 8. "Notes on some Sponges belonging to the Clionidæ obtained at Madeira," by J. Yate Johnson. Exhibition of Wild Flowers with Microscope, by C. Beck.

HANDBOOK OF PATENT LAW.
By W. P. THOMPSON, C.E., F.C.S., &c.
TENTH EDITION, 1896. ADDENDUM, 1898.
The above well known work has just been thoroughly revised, and the large number of alterations made since 1896 in Continental and Foreign Patent Laws have been summarised in an Addendum corrected to December, 1898. Price complete, 2s. 6d.
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THE CHEMICAL NEWS.

Vol. LXXIX., No. 2065.

THE DIFFUSION OF IONS INTO GASES.*

By JOHN S. TOWNSEND, M.A. (Dublin), Clerk Maxwell Student, Cavendish Laboratory, Cambridge.

In the paper upon this subject, the principles upon which the theory of interdiffusion of gases depends, are applied to the diffusion of ions produced by Röntgen rays. When a gas has been left to itself, the conductivity gradually disappears. When no electromotive forces are acting, the loss of conductivity is due partly to positive and negative ions coming into contact with each other, and partly to the effect of the surface of the vessel, which discharges those ions which come into contact with it.

In order to illustrate in a simple way the principles which are involved, we take the case of a gas contained in a metal sphere, and consider what happens to the ions after the gas has been removed from the influence of the rays. For present purposes we may neglect the effect of re-combination.

The ions may be considered as constituting a separate gas, the molecules of which may be either bigger or smaller than the molecules of the gas in which they are immersed. When an ion comes into contact with the surface of the sphere it loses its charge, so that the metal may be regarded as a body which completely absorbs the ions. The reduction in the conductivity by the diffusion of the ions to the sides, is exactly analogous to the removal of moisture from a gas by bubbling it through sulphuric acid. The more rapidly the water vapour diffuses through the gas, the greater will be the number of water molecules which come into contact with the acid round the bubble. If the quantity of moisture which is removed be found experimentally, the coefficient of diffusion of water-vapour into the gas can be deduced (John S. Townsend, *Phil. Mag.*, June, 1898). It would be impracticable to use this method to find the coefficient of diffusion of ions into a gas contained in a large vessel, as the loss of conductivity due to re-combination would be large compared with the loss due to the sides.

The method which was employed was to pass a uniform stream of gas through fine metal tubing, and to allow the rays to fall on the gas immediately before entering the tubing. The bore of the tubing can be so adjusted that the number of ions which come into contact with the sides will be large compared with the number which re-combine. It is convenient to use tubing of such a length that the conductivity will be reduced to about one-half its initial value.

In order to obtain the coefficient of diffusion when the reduction in the conductivity has been found experimentally, the following problem presents itself:—

If a small quantity of a gas, A, is mixed with another gas, B, and the mixture passed along a tube, the sides of which completely absorb A, to find what quantity of A emerges from the tube with B.

It will be immediately seen that if the gases diffuse rapidly into each other, a large proportion of the molecules of the gas A will come into contact with the surface of the tube and will there be absorbed. If, on the other hand, the rate of interdiffusion is very small the molecules of A will travel down the tube in straight lines parallel to the axis of the tube, and practically none of them will come into contact with the surface.

The complete solution of the above problem may be obtained from the following equations:—

$$\frac{1}{\kappa}\rho u = -\frac{dp}{dx} + nXe,$$

$$\frac{1}{\kappa}\rho v = -\frac{dp}{dy} + nYe,$$

$$\frac{1}{\kappa}\rho w = -\frac{dp}{dz} + nZe + \frac{1}{\kappa}\rho W,$$

and the equation of continuity—

$$\frac{d}{dx}(\rho u) + \frac{d}{dy}(\rho v) + \frac{d}{dz}(\rho w) = 0;$$

where n is the number of ions per cubic centimetre; p, their partial pressure; e, the charge on each ion; X, Y, and Z, the electric forces at any point; u, v, and w, the velocities of the ions; W, the velocity of the gas B through the tube; κ, the coefficient of diffusion of the ions into the gas B.

The partial differential coefficient with respect to the time is omitted from the equation of continuity, as we need only consider the steady state.

The term dp/dx may be omitted from the third equation, as it is small compared with the other terms.

$W = \frac{2V}{a^2}(a^2 - r^2)$; where V is the mean velocity of the gas B, defined by the condition $\pi a^2 V t$ = total volume of gas crossing any section in a time t; a the radius of the tube, and r the perpendicular distance of any point from the axis.

The forces X, Y, Z vanish, since the electrification is too small to contribute appreciably to the motion of the ions.

The boundary conditions are—

$p = 0$ when $r = a$,

$p =$ constant when $z = 0$.

The solution of the problem requires a somewhat lengthy analysis, so that we give here only the final result.

The ratio of the number of ions (or molecules of the gas A), coming out of the tube with B to the number which enter is—

$$R = 4[0{\cdot}1952\,\epsilon^{-\frac{7{\cdot}313\,\kappa z}{2a^2V}} + 0{\cdot}0243\,\epsilon^{-\frac{44{\cdot}5\,\kappa z}{2a^2V}} + \&c.],$$

where z is the length of the tube.

The other terms of the series are too small to be taken into consideration.

Having determined the reduction in conductivity due to tubes of different lengths, the following values of the coefficients of diffusion of ions into air, oxygen, carbonic acid, and hydrogen were obtained:—

Table of Coefficients of Diffusion of Ions in Dry Gases.

Gas.	κ for + ions.	κ for − ions.	Mean value of κ.	Ratio of the values of κ.
Air	0·0274	0·042	0·0347	1·54
Oxygen	0·025	0·0396	0·0323	1·58
Carbonic acid..	0·023	0·026	0·0245	1·13
Hydrogen . ..	0·123	0·190	0·156	1·54

Table of Coefficients of Diffusion of Ions in Moist Gases.

Gas.	κ for + ions.	κ for − ions.	Mean value of κ.	Ratio of the values of κ.
Air	0·032	0·035	0·0335	1·09
Oxygen	0·0288	0·0358	0·0323	1·24
Carbonic acid..	0·0245	0·0255	0·025	1·04
Hydrogen . ..	0·128	0·142	0·1350	1·11

We would expect from the experiments that the above numbers are correct to 5 per cent.

Considering one of the equations of motion—

$$\frac{1}{\kappa}\rho u = -\frac{dp}{dx} + nXe,$$

we see that when $dp/dx = 0$, the velocity u due to the

* Abstract of a Paper read before the Royal Society, May 18, 1899.

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electric force X is $nX\epsilon\kappa/p$. If the potential gradient is one volt per centimetre, X = 1/300 in electrostatic units, and the corresponding value of u is—

$$u_1 = \frac{\kappa\epsilon}{300} \cdot \frac{n}{p}.$$

Let N be the number of molecules in a cubic centimetre of a gas at pressure P, equal to the atmospheric pressure, and temperature 15° centigrade, the temperature at which u and κ were determined.

The quotient N/P may be substituted for n/p in the above equation, and since the atmospheric pressure P is 10^6 in C.G.S. units, we obtain—

$$N\epsilon = \frac{3 \times 10^6 u_1}{\kappa}.$$

The following values of $N\epsilon$ thus obtained for different gases are—

Air	$N\epsilon_A = 1{\cdot}35 \times 10^{10}$
Oxygen	$N\epsilon_O = 1{\cdot}25 \times 10^{10}$
Carbonic acid	$N\epsilon_C = 1{\cdot}30 \times 10^{10}$
Hydrogen	$N\epsilon_H = 1{\cdot}00 \times 10^{10}$

The values of u were taken from the table of mean velocities given by Professor E. Rutherford (*Phil. Mag.*, November, 1897). The values of κ which were used are the mean values obtained for dry gases.

Experiments on electrolysis show that one electrodynamic unit of electricity in passing through an electrolyte, gives off 1·23 c.c. of hydrogen at temperatures 15° and pressure 10^6 C.G.S. units. The number of atoms in this volume is 2·46 N, so that if E is the charge on an atom of hydrogen in the liquid electrolyte,—

$$2{\cdot}46\ NE = 1 \text{ electrodynamic unit of quantity} = 3 \times 10^{10} \text{ electrostatic units.}$$

Hence—

$$NE = 1{\cdot}22 \times 10^{10},$$

the charge E being expressed in electrostatic units.

Since N is a constant, we conclude that the charges on the ions produced by Röntgen rays in air, oxygen, carbonic acid, and hydrogen are all the same and equal to the charge on the hydrogen ion in a liquid electrolyte.

Professor J. J. Thomson (*Phil. Mag.*, December, 1898) has shown that the charge on the ions in hydrogen and oxygen which have been made conductors by Röntgen rays, is 6×10^{-10} electrostatic units, and is the same for both gases.

Taking this value for the charge ϵ, we obtain the number of molecules in a cubic centimetre of a gas—

$$N = 2 \times 10^{19}.$$

From this we deduce the weight of a molecule of hydrogen, ρ/N,—

$$4{\cdot}5 \times 10^{-24} \text{ grms.}$$

Since, as we have shown, the charge on an ion produced by Röntgen rays is equal to the charge on a hydrogen ion in a liquid electrolyte, this latter charge is also 6×10^{-10} electrostatic units.

Although the value of $N\epsilon$ for hydrogen is 25 per cent less than its value for other gases, we are justified in including hydrogen in the above general conclusion, as we would expect the value of u for hydrogen to be too small. Professor Rutherford makes no mention of having corrected for the presence of air in his apparatus, or of having used perfectly dry hydrogen. If we take the mean value of κ for moist hydrogen, we obtain $N\epsilon_H = 1{\cdot}15 \times 10^{10}$.

In order to prove that the charge on the positive ion is equal to the charge on the negative ion, the ratio of the coefficients of diffusion must be shown to be equal to the ratio of the velocities. Professor J. Zeleny (*Phil. Mag.*, July, 1898) has shown that the negative ions travel faster under an electromotive force than the positive ions, the ratios of the velocities being 1·24 for air and oxygen, 1·15 for hydrogen, and 1·0 for carbonic acid.

The experiments on diffusion show that the ratio of the velocities would be larger in dry than in moist gases; but as this point has not yet been examined by Professor Zeleny, we cannot expect a very close agreement between the ratios which he gives for the velocities and the ratios of the coefficients of diffusion.

We are led to conclude that the charges on the positive and negative ions are equal from another point of view. It has been proved that the mean charge is the same as the charge on an ion of hydrogen in a liquid electrolyte. If the charges differed, one of them would be less than the charge on the hydrogen ion, whereas experiments on electrolysis show that all ionic charges are either equal to the charge on the hydrogen ion or an exact multiple of it.

GRAPHITE: ITS FORMATION AND MANUFACTURE.*

By E. G. ACHESON, Member of the Franklin Institute.

Early History and Recognition.

In the year 1779, Karl Wilhelm Scheele, a young apothecary in the town of Koping, Sweden, a remarkable genius as an investigator, and then in the 37th year of his age, discovered that graphite had an individuality quite apart from molybdenum sulphide, with which it had been until then confounded. He discovered that when it was treated with nitric acid, carbon dioxide was produced, whereas molybdenum sulphide when oxidised produced a white earth, and he drew the conclusion that it must be some kind of carbon, likely of the general nature of coal.

Previous to this discovery by Scheele, a group of minerals including graphite and certain ores of lead, molybdenum, antimony, and manganese (lead sulphide, molybdenum sulphide, antimony sulphide, manganese dioxide) were believed to be one and the same substance, or, at least, members of the same family. This opinion was due to their outward resemblance, and the fact that they produced marks on paper. This confusion naturally led to the application of the same name or names to each of the members of the group, and as graphite had not been recognised by any peculiarity distinctively its own, it received the names molybdæna, plumbago, graphite, and black-lead, which were used in an indiscriminate manner for each of the several substances. The name molybdæna was dropped at an early date, probably immediately following the discovery by Scheele, and there is no known reason why plumbago and black-lead should not have followed its lead, for graphite is the only one of the series not misleading and entirely appropriate, meaning as it does "I write," from the Greek word γρυφω.

Graphite does not seem to have received any particular attention from chemists from the time of the discovery by Scheele until the year 1800. During the last quarter of the eighteenth century, the diamond was the subject of much interest, in a chemical sense, and in the hands of the French chemists it was shown to produce carbon dioxide when ignited in air. In 1796 Smithson Tannant showed that equal weights of charcoal and diamond yielded equal weights of carbon dioxide on burning, and they were thereafter associated together as carbon. In 1800 Mackenzie added graphite to the carbon group, by showing that it also, in equal weight, produced the same weight of carbon dioxide (Roscoe). Thus, in the opening year of the present century, graphite was proven to be an elementary substance. Charcoal, diamond, and graphite were then recognised as three distinct allotropic forms of the element carbon.

Distribution.

Graphite, in a more or less pure state, is quite freely distributed over the earth, but only in a few places is it

* From Advance Sheets of the *Journal of the Franklin Institute*, June, 1899.

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found under conditions of purity, quantity, ease of mining, refining, and transportation to market that permit of a profitable business being made of it. Statistics for the six years 1890 to 1895, inclusive, give the world's production as 73,751, 57,220, 54,280, 55,810, 46,951 and 53 955 short tons. This is an average yearly production of 56,994 tons —over 156 tons every day of the year—of a material known to the majority of men as black-lead or plumbago, useful only for writing on paper and polishing stoves.

The production during the years mentioned was contributed to by Austria, Ceylon, Germany, Italy, United States, Canada, Japan, India, Russia, Great Britain, and Spain, the proportionate quantities furnished by these countries being in the order given (*Mineral Industry*, 1898). It will be observed that Great Britain is, with but one exception, the smallest producer; indeed 45 tons cover the total amount reported, and this was mined in 1895. For several centuries Great Britain was one of, or the, largest producer; in fact, in the earliest days of the industry, it was probably the only one. The graphite from the Borrowdale mines in Cumberland was famous as the best for making pencils. In the sixteenth and seventeenth centuries these mines were so productive as to yield an annual revenue of £40,000, although they were only worked a few weeks in the year for fear of exhausting them (Roscoe).

Great differences exist in the structure and purity of the graphites furnished from the various mines. Mother Nature was seemingly not content with making carbon appear in three forms, charcoal, diamond, and graphite, but extended her labours on graphite; and, to the further confusion of the metallurgist and the chemist, made it a family of two members, crystalline and amorphous, two distinct allotropic forms of the allotropic substance, graphite. The product of the Ceylon mines is crystalline, of great purity, analysing in some instances over 99 per cent carbon, while that of the Borrowdale mines is amorphous and also very pure.

The chief impurity in graphite is iron; indeed, its constant presence and frequent large quantity led to the belief, in the early days, that graphite was a carbon-iron compound, and it was even sometimes called carburet of iron.

Uses.

It is quite probable that the first use made of graphite was an instrument for writing. The first account we have of its employment for this purpose is contained in the writings of Conrad Gessner on "Fossils," published in 1565. A picture of a pencil is shown, and, referring to it, he says:—"The pencil represented below is made for writing, of a certain kind of lead (which I am told is an artificial substance termed by some, English antimony), sharpened to a point and inserted in a wooden handle" (Roscoe). This pencil was probably made of graphite from the Borrowdale mines, which, we are told, were in operation in the sixteenth century. Its uses for other purposes than pencils are of much more recent date, probably all of them falling within the present century, and nearly all within the last few years.

The present uses of graphite include the manufacture of pencils, crucibles, stove polish, foundry facing, paint, motor and dynamo brushes, anti-friction compounds, electrodes for electro-metallurgical work, conducting surfaces in electro-typing, and covering the surfaces of powder grains. For most of these purposes it is used in the natural impure state, while for others it is necessary to render it quite pure and free from grit. Its purification is accomplished by a method worked out by Brodie, which consists in first grinding, or otherwise reducing the graphite to a state of fine subdivision, washing out the heavier impurities, mixing 14 parts with 1 part of potassium chlorate and 2 parts of concentrated sulphuric acid, heating on a water-bath for some hours, washing thoroughly and afterwards roasting at a red heat. If silica is present a treatment with hydrofluoric acid is added to the process.

The mining and manufacture of graphite into articles for which it has been found useful give employment to thousands of people. The mines of Ceylon alone, when working to their capacity, employ about 24,000 men, women, and children; the work, however, is done entirely by hand, and in a very crude manner (Watts' "Dict. of Chem.," 1890). In the city of Nüremburg, Germany, the home of the famous Faber pencil, are twenty-six factories, employing about 5500 people in the making of pencils ("Encl. Brit.").

Manufacture.

The rapid increase in the use of graphite, and consequent decrease in Nature's stocks, make the problem of manufacturing it to order a subject of much importance.

When we consider the hundreds of thousands of chemical changes men are constantly putting the elementary bodies through, and the very prominent part taken by carbon in these reactions, it would be rather remarkable if at some point, Nature's method for producing graphite was not discovered. That it is not a very difficult act is evident from the fact that it has been accomplished, in a small way, in several instances.

Mr. Muir, in Watts' "Dictionary of Chemistry," edition of 1890, mentions six recognised methods.

(1) By heating charcoal with molten iron, and dissolving out the iron with hydrochloric and nitric acids.

(2) By the slow decomposition of hydrocyanic acid, and boiling the product with nitric acid.

(3) By evaporating the mother-liquors obtained in making soda: these contain cyanogen compounds which are decomposed at a certain concentration of the liquid with formation of ammonia and graphite.

(4) By leading carbon monoxide over ferric oxide at 300° to 400°.

(5) By the decomposition of carbon disulphide at high temperature, in contact with metallic iron.

(6) By leading carbon tetrachloride over molten pig iron.

Whether or not any of these methods could be developed to a state providing a commercial process, I am not prepared to say, but am inclined to think not. They have always been considered accidents or chemical feats of the laboratory, and in some instances their formation was very objectionable.

The Cowles Bros., of Cleveland, O., are reported to have found that graphite sometimes occurred in or about the charge of an electric furnace. This formation is referred to in one of their patents, and a feature of the patent is a provision to get rid of the material, as it was very objectionable on account of its high electric conductivity. Its formation was not reduced to a method, the causes for, or the exact conditions under which it was made, not having been investigated. It was like some of those in the list of Muir, an accident, and a great nuisance.

Still another way of making graphite was described by G. Rose, in 1872. He exposed a cut diamond, bedded in charcoal, to a temperature equal to molten cast iron, whereupon the surface became coated with graphite. It is safe to say this process will never attain commercial success nor popularity.

Finally, in the "Encyclopædia Britannica" (1890) we are told that "by heating to the high temperature afforded by a powerful galvanic battery, both the diamond and amorphous carbon are converted into graphite." This statement I will refer to later on.

In a paper which I had the honour of presenting to the Institute at its stated meeting of June 21, 1893 ("Carborundum: its History, Manufacture, and Uses"), reference was made to the formation of a black material consisting of a mixture of carborundum and free carbon during the operation of the carborundum furnaces. This was again referred to, and at much greater length, by Mr. Francis A. Fitzgerald, chemist to the Carborundum Company, in a lecture delivered before the Institute on December 11th, 1896 ("The Manufacture and Development of Carborundum at Niagara Falls"), after it had been the subject

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of much thought and study, and when I had about concluded the formulation of a theory covering the transformation of amorphous into graphitic carbon.

Very early in my experiments on the manufacture of carborundum, I noticed that graphite occasionally formed in the portion of the furnace charge lying next to the cylinder of granular amorphous carbon, which passed through the centre of the furnace, and which became heated to an extremely high temperature, by the passage of a heavy electric current, and around which the charge was placed to receive the heat necessary for the formation of carborundum. Also that when ordinary bituminous coal coke was used to form the core, quite a large amount of it was converted into graphite, whereas, when petroleum coke was used, very little of it was made graphitic.

By a careful study of these formations, it was found that the graphite formed outside of and surrounding the core was produced by the decomposition of the carborundum, which is, chemically, a carbide of silicon, and, by induction from a number of known facts, that that formed within the core was also produced from a similar decomposition of carbides, which were created by the chemical union of the carbon of the core with its contained impurities. The facts from which I have drawn this conclusion are:—

1. Comparatively pure petroleum coke produces practically no graphite.

2. Impure bituminous coal coke produces large quantities.

3. The larger the known percentage of impurities in the bituminous coal coke, the greater the amount produced.

4. That only a part of the carbon of the core is converted into graphite. This not being increased, even by repeated use of the same grains, in successive carborundum furnaces.

The graphite formed by the destruction of carborundum is remarkable in that it retains the form of the crystal of carborundum from which it is derived. It has, however, less than one-third the weight of carborundum, and possesses the characteristic metallic-grey colour of natural graphite; but in size and form it so closely resembles the original crystal as to be, in fact, its skeleton pseudomorph in graphite. The graphite formed in the core is usually not so well defined, or distinct, as in that from carborundum, most of it being disseminated through the body of the individual grains in which it is found, the amount contained in any one grain varying with the percentage of impurity originally present. In some instances the entire mass of the grain is converted into beautiful graphite, this occurring, I think, in cases where the grain is largely composed of slate, and it sometimes happens that one-half of the grain is completely converted, while the remainder is changed but little.

These two seemingly distinct methods of producing graphite from carborundum and from coke, are, in fact, identically the same; the first step in each is the formation of a carbide, the second its destruction. In making carborundum, silica and coke are mixed in the correct proportions to produce a true carbide, when heated in the electric furnace, without an excess of either constituent In making this mixture, account is taken of the impurities contained in the coke, and the silica reduced proportionately. In the case of the core there is a natural mixture that produces a carbide from a portion of the carbon. The carbides formed under both of these conditions decompose when heated to a certain temperature above that at which they were formed.

This method of manufacturing graphite I would define as consisting in heating carbon, in association with one or more oxides, to a temperature sufficiently high to cause a chemical reaction between the constituents, and then continuing the heating until the combined carbon separates in the free state. It is not, however, limited to the use of oxides, as pure metals; their sulphides and other salts may be used, but for various reasons the oxides are to be preferred.

Theory of Formation.

All of the methods of manufacture, thus far known, contain the same underlying fundamental principle. Each of the six methods described by Muir, as well as my own method, contain as a part of the process the expulsion or liberation of the carbon from a chemical association with one or more elements, and this occurs under conditions unfavourable to, or absolutely prohibitive of, its re-association with the same or other elements. It is cast out, free to take unto itself such physical or other properties as, we must assume, properly belong to it in the free state, when formed under normal conditions. It has been shown by Moissan, that, when subjected to great pressure, at the moment of separation from cast-iron, carbon has those distinctive characteristics that cause it to be called diamond; while Scheele showed, in 1778, that the same carbon, separating from the iron without pressure, takes the graphitic form. Amorphous carbon, the third allotropic form, never occurs pure, and is invariably produced from carbon held in chemical association with other elements, under conditions favourable to free chemical action between it and other elements.

The production of graphite by Rose's method—heating a diamond bedded in charcoal to the melting-point of cast-iron—is a beautiful illustration of the return of a body under strain to the form it takes under normal conditions. It will be noted that the diamond was heated to the temperature at which it is known to form, as shown by Moissan's experiments; also that it was fairly well protected from chemical action.

The statement in the "Encyclopædia Britannica" that both diamond and amorphous carbon are converted into graphite, when heated by a powerful electric current, is very commonly held,—indeed, I might say universally,—although Berthelot concluded, from his investigations, that heat alone is without influence on carbon; that is to say, graphite is not changed to amorphous carbon, nor the amorphous to graphite, when heated to whiteness in an atmosphere of hydrogen or chlorine. That diamond will change to graphite, when protected from chemical influences, under the influences of high temperature, is undoubtedly true, and, indeed, is what might be expected from other known facts; but that *pure* amorphous carbon will change to graphite as the simple result of heating, is not proven, and certainly it does not occur at, or below, the temperature necessary for the transformation of the carbon in a carbide to graphite.

From the facts in hand I have deduced the following theory:—

1. Graphite is the form carbon assumes, when freed from chemical associations, under conditions of low pressure and protection from chemical influence.

2. Diamond is the form carbon assumes, when freed from chemical associations, under conditions of high pressure and protection from chemical influence. And, by inference,—

3. Amorphous carbon is the form carbon assumes, when freed from chemical associations, under conditions of low or high pressure and exposure to chemical influence.

This theory does not, however, account for all of the observed facts, and must be supplemented by the hypothesis that catalysis occurs, under certain conditions, during the transformation of amorphous into graphitic carbon. The amount of graphite produced in the core of a carborundum furnace, and also in graphite articles I have made, is much too great to be accounted for by the theory that it is formed by the dissolution of the fixed carbides, formed by the contained impurities and carbon sufficient to satisfy the chemical formula. The most probable and satisfactory explanation is that a catalytic action occurs—a progressive formation and dissolution of carbides. The temperature being much above the point

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of volatilisation of silica, and all other possible impurities, a rapid dissipation of the active agents takes place, and is completed, in this case, before the conversion of all of the amorphous carbon can occur.

Commercial Manufacture.

As the result of my investigations and deductions, I think the only commercial way to make graphite is by breaking up a carbide by the action of heat, The carbon should be freed from chemical combination by what might be termed the evaporation of its associated elementary substances. I have secured patents covering this method, and these have been made the basis for the organisation ef an incorporated company, bearing the name "Acheson Graphite Company." The company has now under way the erection of works at Niagara Falls, where the necessary electric current will be obtained from the Niagara Falls Power Company.

Several distinct forms of the product will be produced. One consists of forms or articles, made out of amorphous carbon, with the desired amount of impurity added thereto, which will afterwards be heated in an electric furnace, and converted, more or less, into graphite. I have been carrying on this line of manufacture for a year or more, using the furnaces of the Carborundum Company to produce the graphitisation, the articles having first been made by the arc-light carbon manufacturers. Over 200,000 carbon electrodes, measuring 15 inches in length, with about 1 inch cross-sectional area, were made for use in the Castner alkali process, nearly one-half of them having been shipped to Europe, to be used for this work in England and Germany. The life or efficiency of these graphitised electrodes is many times that of the same electrodes ungraphitised. I have also graphitised some tons of carbon plates, to be used in making dynamo and motor brushes, and a large variety of odd forms and sizes for divers purposes.

Another product—the one which will probably be of greatest importance—is an intimate mixture of pure amorphous carbon and graphite in fine powder. This will be put on the market for paint and foundry facing, and, as it has been formed at an extremely high temperature, it is quite pure, and possesses all of the qualities desirable for the purposes for which it is intended.

It is not the present intention of the company to enter into the manufacture of their product into finished form for the general market, but rather to encourage those who are now engaged in making up the natural graphite into articles of commerce to become buyers of their material, substituting it for that now used.

The company's plans, now being carried out, provide for the erection of a brick-and-iron building, 100 × 50 feet, on a plot of ground in Block No. 8 of the Niagara Falls Power Company's lands (adjoining the works of the Carborundum Company). Therein they will erect machinery for reducing coke to grains of the desired size, an electric furnace through which the prepared grains will pass in a continuous stream, a pulveriser for reducing the grains as received from the furnace, and a scalping sieve through which the product from the pulveriser will pass, that particles exceeding the 1/20oth of an inch diameter may be removed. The final flour or powder will contain an amount of pure graphite proportionate to the percentage of impurities in the original coke. It is quite possible that, instead of using high-grade marketable coke, the fine refuse from the coke ovens—which is at present a waste material—will be utilised in the manufacture of this product.

In this connection I would call attention to the need of a specific name for the new product. *Artificial*, as applied to a product, chemically and physically identical with that made by Nature, is not pleasing: it conveys the impression that, failing to produce the real thing, a cheap imitation, a sham, is being palmed off as the genuine article. Not even the Century Dictionary's definition of artificial, as "made or contrived by art, or by human skill and labour; opposed to Nature," is sufficient to banish this feeling; for, after all, in the particular case in hand, being ignorant of the exact methods pursued by Nature, we may be simply forcing her to reveal her methods, to the final results of which we neither add nor subtract one jot or tittle. The same objections may be made to the expression *Artificial Manufacture* of Graphite, for we may not be sure that the process forced upon her is not identical with that of her own selection. *Manufactured Graphite* would be quite appropriate, were it not for the fact that it is popularly applied to articles made of graphite.

It may not detract from the general interest in this subject to call attention, in closing, to the fact that graphite, first shown to be an elementary body, an allotropic form of carbon, in the first year of the nineteenth century, is in this, the last year, made to order in great quantities, and that it will, before the close of the century, become an article of ordinary commerce in its new form. Perhaps it will take its place as the primitive form of carbon—the one it assumes under normal conditions.

METATHETIC REACTIONS BETWEEN CERTAIN SALTS IN SOLUTION IN LIQUID AMMONIA.

By E. C. FRANKLIN and C. A. KRAUS.

THE great power of anhydrous ammonia as an electrolytic solvent, occupying as it does, of all known solvents, a position nearest to water in its power of dissociation (Cady, *Journ. Phys. Chem.*, 1897, i., 707) and in its capacity as a general solvent (*Amer. Chem. Journ.*, xx., 820), has led the authors to enquire whether or not metathetic reactions, similar to those which take place in aqueous solutions, do not take place also in ammonia solutions. If salts in solution in ammonia are dissociated to an extent approximating the dissociation in water solutions, then salts insoluble in ammonia should be precipitated rapidly and completely when ammonia solutions of salts containing the ions necessary for the formation of such substances are brought together. That in a considerable number of cases such action takes place is shown by the experiments described in this paper.

Method of Making the Tests.

The nitrates of sixteen metals, selected because of their ready solubility, together with the fact that they were at hand, were chosen to furnish the metallic ions, while the sulphide, chloride, bromide, iodide, chromate, and borate of ammonium constitute the list of salts which were used as precipitants.

The tests were made by bringing together in a small vacuum-jacketed test-tube solutions of the nitrate and of the precipitant, and observing whether or not a precipitate was formed.

General Results.

Ammonium Chloride as Precipitant (Table I.).—Most of the metals tested are precipitated as chlorides by the action of ammonium chloride. Those chlorides which by direct experiment were found to be entirely insoluble, separate immediately and completely when the two solutions are brought together, while those which were found to be slightly or but moderately soluble, separate slowly and incompletely from more concentrated solutions.

Ammonium Bromide as Precipitant.—Table II. gives the results obtained by the use of ammonium bromide as precipitant. As was to be expected, considering the greater solubility of the bromides, these precipitates formed more slowly than the corresponding precipitates of chlorides.

Ammonium Iodide as Precipitant (Table III.).—Corre-

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sponding with the much greater general solubility of the iodides, but two metals, barium and strontium, gave precipitates with ammonium iodide, and even these, as the crystalline nature of the precipitates indicates, are probably very slightly soluble.

Ammonium Sulphide as Precipitant (Table IV.).—A solution of ammonium sulphide was prepared by passing washed and dried hydrogen sulphide into liquid ammonia. The gas dissolved, forming a clear colourless solution. Ammonium sulphide was also prepared by the action of liquid anhydrous ammonia on liquid hydrogen sulphide. To the hydrogen sulphide at the temperature of the carbon dioxide and ether bath, liquid ammonia was added, with the result that immediately a mass of white solid ammonium sulphide was formed. Excess of ammonia dissolved the solid to a clear solution. On cooling the solution, saturated at the boiling temperature of ammonia, to the temperature of the carbon dioxide and ether bath, there was an abundant separation of crystals. A small quantity of these crystals, as well as a larger quantity of the white solid, were filtered off, freed from ammonia, and transferred to a specimen tube. Although no analysis of the solid was made, there can be scarcely any doubt of its identity as ammonium sulphide.

All the metals tested, with the exception of the alkalis, gave precipitates with ammonium sulphide. Only a portion of these precipitates, however, as their most obvious property, their colour, indicates, can be identical with the precipitates formed in aqueous solutions. Certainly the lead precipitate, after removing it from the solution and drying it at the laboratory temperature, is lead sulphide. The remaining black precipitates have not been studied. The precipitates formed from barium, strontium, calcium, and magnesium solutions are especially interesting for the reason that these metals in aqueous solution give no precipitates with ammonium sulphide. It is the expectation of the authors to collect and analyse these four precipitates, but up to the present this has been accomplished in the case of but one of them, and this with not entirely satisfactory results.

Magnesium-ammonium Sulphide, $2MgS.(NH_4)_2S.xNH_3$.

Preparation.—To a Dewar test-tube containing a fairly strong solution of magnesium nitrate, an ammonia solution of ammonium sulphide was added as long as a precipitate continued to be formed. In order to separate the precipitate from the liquid, the contents of the tube were poured upon a filter, of which the following is a description. In the figure, A is the filtering funnel proper, consisting simply of a thin-walled tube of the shape and size indicated, and provided with a platinum Witt filtering plate, *b*. The filtering tube is held in place by means of corks at *c* and *d*; *e* is a vacuum-jacketed tube. The space *f* is filled with ammonia to a convenient height.

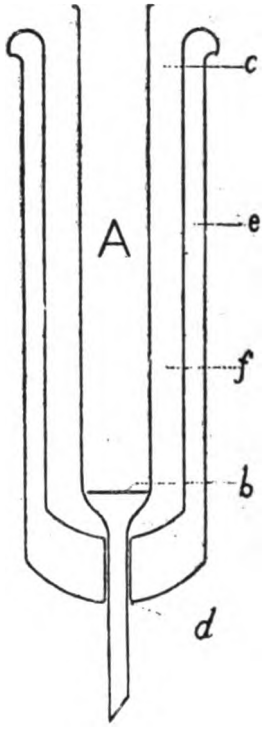
The precipitate, after being transferred to the filter, was washed several times with fresh quantities of ammonia, the filtration being accelerated by closing the mouth of the tube by means of a cork. The pressure of the supernatant gas forces the wash-fluid through rapidly. After sufficient washing, the tube was removed from the ammonia-bath, both ends were closed, one of them by means of a cork carrying a drying tube filled with soda-lime, and the ammonia allowed to pass off at the ordinary temperature.

Properties of the Precipitate.—The compound was a finely crystalline white solid, which gave off the odours of ammonia and hydrogen sulphide at the laboratory temperature. Freshly prepared, it is completely soluble in water. After standing for a short time exposed to the air, it was no longer entirely soluble—a result due undoubtedly to the formation of magnesium hydroxide by the action of the moisture and oxygen of the air.

Analysis of the Precipitate.—Portions of the compound, prepared as described above, were transferred as rapidly as possible to small weighing tubes. These were weighed and dropped into bottles containing fuming nitric acid. The sulphuric acid formed and the magnesium were determined according to the usual methods. The following results were obtained:—

	I.	II.	III.
Weight of substance	0·1691	0·1906	0·2780
Magnesium pyrophosphate.	0·1171	0·1266	0·1793
Barium sulphate..	0·3166	0·3954	0·5828
Magnesium	0·0231	0·0274	0·0387
Sulphur	0·0435	0·0537	0·0794
Per cent magnesium	13·60	14·44	13·92
„ sulphur..	25·70	28·19	28·37

These determinations, made each on a different specimen of the substance, indicate in the material analysed the presence of two atoms of magnesium to three atoms of sulphur with varying quantities of ammonia. The results obtained probably harmonise best with the assumption that the compound is a double sulphide of ammonium and magnesium, containing two molecules of magnesium



sulphide and 1 molecule of ammonium sulphide, together with ammonia of crystallisation, which, being gradually given off at temperatures above the dissociation-point of the compound, is a sufficient explanation of the variable composition as found by analysis.

The calculated percentage composition of—

$2MgS.(NH_4)_2S.9NH_3$

is—Magnesium 14·41 per cent, sulphur 28·82 per cent, ammonia 56·16 per cent; of $2MgS.(NH_4)_2S.10NH_3$ is—Magnesium 13·71 per cent, sulphur, 27·42 per cent, ammonia 58·28 per cent.

Ammonium Chromate as Precipitant (Table V.).—Chromic acid, which presumably goes into solution as ammonium chromate, dissolves sparingly. Its solution gives precipitates with all the metals tested with the exception of lithium and sodium.

Ammonium Borate as Precipitant (Table VI.).—Boracic acid, which in solution in ammonia presumably forms am-

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monium borate, is but sparingly soluble. Its solution gives precipitates with all the metals tested with the exception of lithium, sodium, and potassium.

TABLE I.—*Ammonium Chloride as Precipitant.*

Salt.	Remarks.
Lithium nitrate.. ..	Precipitate, from concentrated solution.
Sodium nitrate	No precipitate.
Potassium nitrate ..	Precipitate, from concentrated solution.
Calcium nitrate . ..	Precipitate, immediate.
Strontium nitrate ..	" "
Barium nitrate	" "
Magnesium nitrate ..	" "
Zinc nitrate	" "
Manganese nitrate ..	Precipitate, immediate, white.
Cobalt nitrate	" " "
Nickel nitrate	Precipitate, immediate, light violet.
Cadmium nitrate ..	Precipitate, immediate.
Mercuric nitrate ..	No precipitate.
Lead nitrate	Precipitate, from concentrated solution.
Silver nitrate	Precipitate, from concentrated solution.
Copper nitrate	Precipitate, from concentrated solution, blue.

TABLE II.—*Ammonium Bromide as Precipitant.*

Salt.	Remarks.
Lithium nitrate.. ..	Precipitate, from most concentrated solutions.
Sodium nitrate	No precipitate.
Potassium nitrate ..	No precipitate.
Calcium nitrate . ..	Precipitate, immediate.
Strontium nitrate ..	Precipitate, immediate.
Barium nitrate	Precipitate, immediate.
Magnesium nitrate ..	Precipitate, not immediate.
Manganese nitrate ..	Precipitate, immediate.
Zinc nitrate	Precipitate, not immediate.
Cobalt nitrate	Precipitate, immediate, white.
Nickel nitrate	Precipitate, immediate, light violet.
Cadmium nitrate ..	Precipitate, immediate.
Mercuric nitrate ..	No precipitate.
Lead nitrate	Precipitate, from concentrated solution.
Silver nitrate	Precipitate, from concentrated solution.
Copper nitrate	Precipitate, from concentrated solution, blue.

TABLE III.—*Ammonium Iodide as Precipitant.*

Salt.	Remarks.
Lithium nitrate.. ..	No precipitate.
Sodium nitrate	No precipitate.
Potassium nitrate ..	No precipitate.
Calcium nitrate . ..	No precipitate.
Strontium nitrate ..	Precipitate, crystalline.
Barium nitrate	Precipitate, crystalline.
Magnesium nitrate ..	No precipitate.
Zinc nitrate	No precipitate.
Manganese nitrate ..	Precipitate, slowly.
Cobalt nitrate	No precipitate.
Nickel nitrate	No precipitate.
Cadmium nitrate ..	Precipitate, slowly.
Mercuric nitrate ..	No precipitate.
Lead nitrate	No precipitate.
Silver nitrate	No precipitate.
Copper nitrate	No precipitate.

TABLE IV.—*Ammonium Sulphide as Precipitant.*

Salt.	Remarks.
Lithium nitrate.. ..	No precipitate.
Sodium nitrate	No precipitate.
Potassium nitrate ..	No precipitate.
Calcium nitrate ..	Precipitate, not immediate, white.
Strontium nitrate ..	Precipitate, immediate, white.
Barium nitrate	Precipitate, immediate, white.
Magnesium nitrate ..	Precipitate, not immediate, crystalline, white.
Zinc nitrate	Precipitate, immediate, white.
Manganese nitrate ..	Precipitate, immediate, white, dissolves on addition of water.
Cobalt nitrate	Precipitate pinkish, on the addition of water the precipitate turns black.
Nickel nitrate	Precipitate white, dissolves on addition of water.
Cadmium nitrate ..	Precipitate white, on addition of water the precipitate becomes yellow.
Mercuric nitrate ..	Precipitate, immediate, black.
Lead nitrate	Precipitate, immediate, black.
Silver nitrate	Precipitate, immediate, black.
Copper nitrate	Precipitate yellowish brown, from concentrated solutions.
Bismuth nitrate ..	Precipitate, immediate, black.

TABLE V.—*Ammonium Chromate as Precipitant.*

Salt.	Remarks.
Lithium nitrate.. ..	No precipitate.
Sodium nitrate	No precipitate.
Potassium nitrate ..	Precipitate, slight, flocculent.
Calcium nitrate . ..	Precipitate, flocculent.
Strontium nitrate ..	
Barium nitrate	
Magnesium nitrate ..	
Zinc nitrate	
Manganese nitrate ..	
Cobalt nitrate	
Nickel nitrate	
Cadmium nitrate ..	
Mercuric nitrate ..	
Lead nitrate	
Silver nitrate	
Copper nitrate	

TABLE VI.—*Ammonium Borate as Precipitant.*

Salt.	Remarks.
Lithium nitrate.. ..	No precipitate.
Sodium nitrate	
Potassium nitrate ..	
Calcium nitrate.. ..	Precipitate.
Strontium nitrate ..	
Barium nitrate	
Magnesium nitrate ..	
Zinc nitrate	
Manganese nitrate ..	
Cobalt nitrate	
Nickel nitrate	
Cadmium nitrate ..	
Mercuric nitrate ..	
Lead nitrate	
Silver nitrate	
Copper nitrate	

—*American Chemical Journal*, xxi., No. 1.

A Common Error in Recorded Results of Proximate Plant Analysis.—Lyman F. Kebler (*Am. J. Pharm.*, lxxi., 25).—The author calls attention to the error caused by adding the percentage of ash to the percentage of the other constituents instead of estimating it in the dried residue left after the action of the various solvents.

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A NEW COMMERCIAL METHOD FOR THE MANUFACTURE OF TARTARIC ACID.

By Dr. G. SCARLATA.

TARTARIC acid occupies one of the most important places among chemical products. It is found in abundance in the form of acid tartrate of potassium and neutral tartrate of lime, in the raw tartar from casks, in wine lees, and in grape skins, which, by the way, constitute the only raw materials used for its extraction.

It is curious to note that, at the present time, the extraction of tartaric acid is almost entirely carried on in England, the United States, and Germany, the wine-producing countries possessing only a few factories of little importance, limited to the treatment of raw material produced on the spot, though more often—in fact nearly always—the stocks are allowed to accumulate, and are then shipped to some foreign factory.

The method of extraction at present used in most factories is very old, viz., that of Scheele. Only very slight modifications have been introduced into this method, while nearly every other chemical industry has undergone radical changes; one fact is certain, that there has been no improvement made in the manufacture of tartaric acid.

I have been attracted to this remunerative industry with the hope of devising a plan by which the English and German methods can be efficiently combined. I have therefore sought principally for an economical method which would not require too much capital to establish in the first place.

The results I have obtained in the laboratory lead me to hope that I have attained the desired result. I leave to practical experience the task of justifiying my opinions.

The first part of Scheele's process consists in obtaining tartrate of calcium. This can be done by different methods, but they are all long and delicate. The methods of Scheurer-Kestner, of Gladysz, of Dietrich, and of Schutzner, all require a considerable amount of time and fuel; the same can be said of the second part of the process, which consists of decomposing the tartrate of calcium with sulphuric acid. This operation yields no useful by-product, and does not allow of the recovery of any of the materials first used.

These drawbacks do not exist in the new method which I propose to use, since by its means we are enabled to extract the tartaric acid directly from the raw product, and to recover the materials used in the operation.

This method, broadly speaking, is based on the decomposition of the tartrates by fluosilicic acid. In the raw product the tartaric acid exists both as acid tartrate of potassium and as tartrate of calcium. These salts are decomposed by fluosilicic acid, with the formation of tartaric acid and of the corresponding fluosilicates.

$$2C_4H_5O_6K + H_2SiFl_6 = 2C_4H_6O_6 + K_2SiFl_6$$
$$C_4H_4O_6Ca + H_2SiFl_6 = C_4H_6O_6 + CaSiFl_6.$$

Tartaric acid and fluosilicate of calcium are both soluble and remain in the clear solution, while the fluosilicate of potassium is to a great extent precipitated; its solubility is only 1 part in 825 parts of water. By evaporating the clear solution the last portions of the fluosilicate of potassium are precipitated very rapidly. There now remains only the fluosilicate of calcium to be eliminated, of which the quantity present is first determined by analysis. The calculated quantity of sulphuric acid is then added, plus a little excess, as tartaric acid crystallises much better in solutions made slightly acid with sulphuric acid. After concentration to help the deposit of sulphate of lime, the organic matter, and the last traces of fluosilicate of potassium, the clear solution is decanted and allowed to crystallise.

We thus obtain fluosilicate of potash as principal by-product; it is found mixed with silica for reasons which will be shown later on, and constitutes an excellent material for the preparation of fluosilicic acid; in fact, by treating it with sulphuric acid, we obtain sulphate of potassium, hydrofluoric acid, and fluoride of silicon, according to the equation—

$$K_2SiFl_6 + H_2SO_4 = SiFl_4 + 2HFl + K_2SO_4.$$

But hydrofluoric acid in the presence of silica gives fluoride of silica and water:—

$$4HFl + SiO_2 = SiFl_4 + 2H_2O.$$

So that the whole of the fluorine from the fluosilicate of potassium is brought to the state of fluoride of silica, which, by reacting on water, gives fluosilicic acid and silica according to the equation—

$$3SiFl_4 + 4H_2O = 2H_2SiFl_4 + Si(OH)_4.$$

As can be seen, the recovery of the fluosilicic acid is complete by a simple treatment with sulphuric acid.

Preparation of Tartaric Acid.

I am not able to describe in detail the apparatus necessary for the manufacture of tartaric acid, but will confine myself to the description of the experiments made with the ordinary apparatus found in the laboratory.

The tartar I used contained by analysis:—

Total tartaric acid	62·56	per cent.
Tartrate of potassium ..	67·16	,,
Tartrate of calcium.. ..	11·25	,,

I operated on 10 kilogrms. of well broken-up material, placed in a wooden vat furnished with a stirrer. To these 10 kilogrms. of raw material I added the quantity of fluosilicic acid theoretically necessary to set all the tartaric acid at liberty,—that is to say, 58 kilogrms. of a solution at 60 per cent. After agitating for an hour, the mixture was transferred to a filter-press, and the clear solution was led into a wooden vat lined with lead and heated by a current of steam passing through a spiral tube. The evaporation was continued until fluosilicate of potassium commenced to be deposited. The contents of the vat were then left alone for some hours, after which the clear solution was decanted into another vat furnished with a stirrer. The lime was estimated on a sample of the solution, by adding an excess of oxalate of ammonia and titrating the excess of oxalic acid by permanganate of potash. The total quantity of solution contained 209 grms. of lime. To eliminate this the solution was treated with the theoretical quantity of sulphuric acid,—that is 512 grms. H_2SO_4 diluted to 1 litre, then transferred to the filter-press.

The solution of tartaric acid thus obtained was coloured a deep reddish brown; after decolourising by animal-black, it was evaporated and crystallised, care being taken to remove the sulphate of lime which is again precipitated at the commencement of the evaporation.

The purity of the crystals of tartaric acid thus obtained was determined by titrating with potash and comparing it with a chemically pure sample of the same acid. It is evident that, in this kind of test, equality of results indicates equality of purity. The results obtained were as follows:—

Tartaric acid at 100 per cent.		Tartaric acid from the experiment.
I.	35·0 c.c. of solution of KOH.	I. 34·5 c.c. of solution of KOH.
II.	41·0 ,, ,, ,,	II. 40·5 ,, ,, ,,
III.	33·0 ,, ,, ,,	III. 32·5 ,, ,, ,,
IV.	36·0 ,, ,, ,,	IV. 35·5 ,, ,, ,,

These figures show that the tartaric acid obtained by the fluosilicic acid process titrated 98·57 per cent of purity; it may therefore be considered as commercially pure.

Preparation of the Fluosilicic Acid necessary for the Operation.

Description of the Apparatus.—This consists of a cast-iron pot fitted with a mechanical stirrer, in which the raw

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material obtained as a by-product from the above reaction is placed. The calculated quantity of concentrated sulphuric acid is added, the cover is luted on, and the whole heated and stirred continuously. The cover has two tubes passing through it; the first—which is for passing a current of air through at the end of the operation—is kept closed by means of a tap during the first phase of the operation; the second—which is much larger—is for the purpose of passing the fluoride of silicon into a vessel filled with water. The water necessary for the decomposition of the fluoride of silicon is added, the quantity is estimated approximately by the quantity of fluosilicate of potash present, so that the solution of fluosilicic acid can be prepared of practically any desired strength. The fluoride of silicon, on entering the vessel, comes in contact with the water, which decomposes it into fluosilicic acid and gelatinous silica.

As a secondary product of this preparation, we obtain sulphate of potassium, which, mixed with the residues from the first operation, forms excellent manure. In any case its intrinsic value will always cover a part of the expense of the process.

As can be seen, this method has the double advantage of being very rapid, and of returning in a useful form all the materials originally used. — *Moniteur Scientifique*, Series 4, vol. xiii., May, 1899.

ON THE DOUBLE CHLORIDES AND BROMIDES OF URANIUM.

By J. ALOY.

Double Alkaline Uranous Chlorides.

Both the uranous chloride, UCl_4, and the uranous bromide, UBr_4, have a strong tendency to unite with the chlorides and bromides of the other metals. Nevertheless the only compound of this order known up to the present was the double chloride of uranium and sodium, $UCl_4.2NaCl$, by the use of which M. Moissan was enabled to obtain pure metallic uranium (*Comp. Rend.* cxxii., 1089). This compound is prepared by the direct action of the vapours of uranous chloride on melted chloride of sodium at a dull red heat. I have, in the same manner, prepared compounds of uranous chloride from the chlorides of potassium and lithium. The experiment is carried out in a Bohemian glass tube in a laboratory gas furnace; the uranous chloride is produced at one end of the tube by the action of chlorine on carbide of uranium, and then passed over the well-dried alkaline chloride placed in a series of boats, heated to dull redness. Under these conditions the chloride, UCl_4, combines with the alkaline chloride contained in the first of these boats, and soon the mass melts by reason of the formation of the double chloride; the action then spreads successively to the other boats.

We could, in this experiment, replace the carbide of uranium by a mixture of oxide of uranium and carbon; it would, however, in such a case, be necessary to greatly increase the temperature of the mixture, and therefore use a very hard, and well protected glass tube.

Whatever the method of preparation, the compounds thus formed correspond to the formulæ $UCl_4.2KCl$ and $UCl_4.2LiCl$.

In appearance they differ but slightly from the double chloride of sodium and uranium described by M. Moissan.

Coloured pale green at the moment of their formation, they soon become dark green on contact with the air from which they absorb the moisture. Much more stable than uranous chloride, these double chlorides, are, however, very greedy for water; their solution, of a beautiful green colour, is effected with a rise of temperature, and possesses a strongly acid reaction.

When very dilute and gently heated, this solution becomes brown like that of uranous chloride; it oxidises slowly in the air, and it requires several days for the oxidation to be complete. Evaporated *in vacuo* over sulphuric acid, it deposits, even in the presence of an excess of uranous chlorides, crystals of alkaline chloride and an uncrystallisable green mass soluble in water. This result, which is due to the dissociation of the compound by water with the liberation of hydrochloric acid, explains the want of success of some chemists who have tried to prepare the pure double chlorides by mixing the two component parts. Ordinary alcohol also exercises a dissociating action, and gives a green solution, which quickly becomes yellow while oxidising; when exposed to sunlight, this solution rapidly becomes brown. The double alkaline uranous chlorides are very soluble in acetic acid.

Double Alkaline-earthy Uranous Chlorides.

The alkaline-earthy chlorides also possess the property of uniting, under the same conditions, with uranous chloride. But the experiment always requires certain precautions; it is necessary, in order to obtain a definite compound, to thoroughly dry the chlorides in a current of dry hydrochloric acid, and not to raise the temperature of the boats to too high a point: by proceeding in this manner the uranous chloride unites with the alkaline-earthy chlorides, giving a fusible compound corresponding to the formula $UCl_4.M''Cl_2$, where M'' represents the alkaline-earthy metal: barium, strontium, calcium.

These double chlorides possess a deeper green colouration than that of the corresponding alkaline chlorides.

In the same manner as these latter they are dissociated by water, and will not crystallise in a dry vacuum.

Double Uranous Bromides.

Uranous bromide, UBr_4, also forms double bromides with the alkaline bromides. I have obtained compounds of potassium and sodium by acting on the alkaline bromide, heated to redness by vapour of uranous bromide.

The bromide, UBr_4, is produced by the action of pure bromine, very carefully dried by means of chloride of calcium, on a mixture of equal parts of green oxide of uranium and carbon. The experiment is made in a porcelain tube heated to bright redness, or in a very hard glass tube, well protected at the part containing the mixture; the bromine is carried in by a current of dry carbonic acid; as soon as the fumes of uranous bromide appear the currrent of gas is increased, the bromine combines with the alkaline bromide which it colours; the mass then melts, and, if the experiment is sufficiently prolonged, the compounds produced correspond to the formulæ $UBr_4.2KBr$ and $UBr_4.2NaBr$. These bromides are of a deeper green than the corresponding chlorides, and possess analogous properties.

In these experiments I was not able to make use of carbide of uranium, which decomposes carbonic acid, giving uranic oxide.

The alkaline-earthy bromides of barium, calcium, and strontium also combine with uranous bromide.

Double Subchlorides of Uranium.

The double subchlorides of uranium and the alkaline metals which have up to the present only been prepared in the wet way, can also be obtained by direct action. By passing a current of dry chlorine over gently heated protoxide of uranium, we obtain the subchloride of uranium; if we increase the temperature as soon as the transformation of the oxide is complete, and increase the current of chlorine, the subchloride of uranium can be carried over and combined with the alkaline chlorides, with which they give fusible compounds of a beautiful golden-yellow colour, the study of which I am pursuing. In a forthcoming paper I shall complete the history of these compounds, and describe some other complex compounds of uranium. — *Bull. Soc. Chim.*, Series 6, vol. xxi., No. 6.

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ON CHLORATED EXPLOSIVES.

By BERGÈS CORBIN.

The method of manufacturing explosives described in this paper consists in mixing the chlorate with nitrated or nitric derivatives dissolved in certain oils.

Picro-naphthalene, for example, is prepared by gradually adding 1·320 kilos. of picric acid, in small portions at a time, to 1 kilo. of melted mononitro-naphthalene. The compound thus obtained melts at 74° C., and dissolves in castor oil in the proportion of 5 per cent in the cold and 80 per cent when warmed (100° C.). At 105° to 110°, 20 grms. of castor oil will dissolve as much as 20 or 30 grms. of this substance.

Picro-nitrobenzene, which is prepared in an analogous manner, melts at 88° and dissolves in castor oil in the following proportions:—

6 to 7 per cent	.. ..	In the cold.
40 ,,	.. ..	At 100°.
100 ,,	.. ..	Above 100°.

The picrates of amidoazobenzene, azobenzene, azoxybenzene, as well as the picrates of the nitrodiphenylamines, have practically the same solubilities in castor oil as the azo-derivatives from which they were formed. The picro-azoic derivatives are obtained by dissolving the nitro-compounds in castor oil at 80° to 100°, and gradually adding picric acid. The solutions thus obtained may be heated well above the temperature at which the nitric derivatives used decompose. Even at 200° no explosion occurs, neither are they decomposed. As a general rule the picric acid can be replaced by picramic acid.

In a similar manner we can prepare compounds containing nitrobenzene and the nitronaphthalenes, and, thanks to the presence of the first of these bodies, we can dissolve a larger proportion of the second in oil; for example, 20 grms. of an animal or vegetable oil will, in the cold, only dissolve 5 grms. of nitronaphthalene, while 10 grms. of the same oil containing 10 grms. of nitrobenzene will dissolve 10 grms. of nitronaphthalene.

To prepare chlorated explosives, the simple or mixed nitrated or nitric derivatives are dissolved in a suitable oil, gradually heated, and the solution mixed with powdered starch or wood charcoal, if one of these substances is required; finally, the chlorate or perchlorate is added in small portions at a time, and the mixing continued until the mass is perfectly homogeneous.—*Zeit. Angew. Chem.*, 1898, xlvii., 1091.

THE ELECTROLYSIS OF ALKALINE CHLORIDES.

By H. WOHLWILL.

The author, considering chloride of sodium to be typical of the alkaline chlorides, selected it for studying its decomposition by electrolysis.

Besides the usual formation of caustic alkali at the cathode, and of chlorine at the anode, we know that certain other reactions take place during the course of the electrolysis, reactions which give rise to the formation of oxygenated acid salts of chlorine. The principal of these salts are the hypochlorites, the chlorates, and—under certain peculiar conditions—the perchlorates.

A question which has both a practical and theoretical interest is that of knowing how a solution originally containing only the anions $\overline{Cl}$, $\overline{OH}$ and O, becomes charged with the constitutive anions of the hypochlorites and the chlorates,—that is to say, $\overline{ClO}$ and ClO_3.

In order to solve this problem, the author has adopted the experimental method proposed by Glaser for studying the electrolysis of aqueous solutions in general. The same problem has been attacked by Oettel and indirectly by Haber; but the intention of the author being to isolate the primary reactions, he took the precautions necessary for observing the initial tendency of these reactions, and not the ultimate products of the electrolysis, as was done by Oettel and Haber.

According to the author, the principal objections which can be made to the methods of his predecessors are the following:—The duration of the experiment is too long; the products of the electrolysis are not separated one from the other, and consequently may be further affected by the current; the composition and concentration of the liquid are essentially variable; &c. By removing these unfavourable conditions, by which simply the sum of the different reactions are given, without allowing any particular one to be characterised, the author has arrived at the following conclusions:—

1. With an electromotive force not exceeding 1·2 volts, a hypochlorite is formed; with an electromotive force of from 1·2 to 1·3 volts, the reaction is almost quantitative, apparently according to the equation—

$$Cl + \overline{O}\ (++) = \overline{ClO}.$$

2. Above 2·1 volts the formation of the hypochlorite is more accentuated on account of the secondary reaction of the liberated chlorine on the alkali present.

3. The chlorate is formed by the reaction of ions susceptible of furnishing positive electricity,* and not by the direct union of the ions $\overline{Cl}$ and $\overline{HO}$, as was admitted by Haber. It is much more probable that the reaction is expressed by the formula—

$$2\overline{ClO} + \overline{OH}\ (++) = ClO_3H + \overline{Cl},$$

in which ClO represents the ions of the hypochlorous acid already formed in the solution.—*Zeits. f. Elektrochemie*, v. (5), p. 52.

ON A NEW METHOD OF FORMING CUPROUS CYANIDE.

By HENRI VITTENET.

We heat a mixture of—

Neutral acetate of copper	15 grms.
Ammonia at 21° B.	30 ,,

in a sealed tube for two hours at a temperature of 180—185°.

The solution is almost entirely decoloured, and carries in suspension a mixture of very fine spangles of metallic copper and of opaque white crystalline flakes. On opening the tube no pressure was noticed. We filtered on a filter-pump; the liquid immediately took a blue colour. The precipitate was washed on the filter with distilled water until it entirely lost its blue colour, and was then digested with water slightly acidulated with H_2SO_4, so as to dissolve the metallic copper.

There thus remained the opaque white flakes, which, when heated to redness on a sheet of platinum, gave a red deposit of copper; they are soluble in boiling dilute hydrochloric acid, in cyanide of potassium, insoluble in dilute boiling sulphuric acid, soluble in nitric acid (giving a green liquid), soluble in concentrated boiling ammonia (giving a blue solution). They give off ammonia when calcined with soda-lime. In short, we have identified this body with the cuprous cyanide obtained by precipitation by adding a hydrochloric solution of cuprous chloride to a solution of cyanide of potassium.

* The expressions *positive* and *negative* electricity, which had completely disappeared from scientific language, have been revived by German electrochemists following the work of Arrhenius on electrical dissociation. They are further in harmony with the modern theories of electrolysis.

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Analysis has given the following results:—

I. Material taken, 0·3064 grm.

Water	0·112 grm.
CO_2	0·1475 ,,
CuO	0·2674 ,,

II. Material taken, 0·2185 grm.

N .. .. .. 29 c.c. at 19°, 763·35 m.m.

Or in parts per cent—

	Found. I.	Found. II.	Calculated for $Cu_3C_2N_2$.
C	13·12	—	13·48
H	0·40	—	0·00
Cu	69·79	—	70·78
N	—	15·27	15·73

The blue liquid resulting from the reaction is treated with 100 c.c. of alcohol at 93°, and set to crystallise in the cold under an exsiccator. It deposits blue needles, which give all the reactions of carbonate of copper.

The cyanogen group is formed by the union of the ammoniacal nitrogen and the carbon of the acetic acid.

The theoretical equation is difficult to express in view of the copper and carbonate of copper mentioned. Doubtless other unnoticed products were formed at the same time.—*Bull. Soc. Chim.*, Series 3, xxi., No. 6.

LONDON WATER SUPPLY.

REPORT ON THE COMPOSITION AND QUALITY OF DAILY SAMPLES OF THE WATER SUPPLIED TO LONDON FOR THE MONTH ENDING MAY 31ST, 1899.

By SIR WILLIAM CROOKES, F.R.S.,
and
PROFESSOR DEWAR, F.R.S.

To MAJOR-GENERAL A. DE COURCY SCOTT, R.E.,
Water Examiner, Metropolis Water Act, 1871.

London, June 10th, 1899.

SIR,—We submit herewith, at the request of the Directors, the results of our analyses of the 208 samples of water collected by us during the past month, at the several places and on the several days indicated, from the mains of the London Water Companies taking their supply from the Thames and Lea.

In Table I. we have recorded the analyses in detail of samples, one taken daily, from May 1st to May 31st inclusive. The purity of the water, in respect to organic matter, has been determined by the Oxygen and Combustion processes; and the results of our analyses by these methods are stated in Columns XIV. to XVIII.

We have recorded in Table II. the tint of the several samples of water, as determined by the colour-meter described in previous reports.

In Table III. we have recorded the oxygen required to oxidise the organic matter in all the samples submitted to analysis.

Of the 208 samples examined by us during the month, all were found to be clear, bright, and well filtered.

The rainfall at Oxford during this month shows a considerable deficit; the actual fall has been 1·37 inches, spread over 11 days; the average fall for May is 1·83 inches, making a deficit of 0·46 inch; this brings the deficit for the year to 0·69 inch, or 7·7 per cent on the thirty years' average.

Our bacteriological examinations of 382 samples have given the results recorded in the following table; we have also examined 40 other samples, from special wells, standpipes, &c., making a total of 422 samples in all:—

	Microbes per c.c.
New River, unfiltered (mean of 26 samples) ..	430
New River, filtered (mean of 77 samples) ..	15
Thames, unfiltered (mean of 26 samples) ..	3247
Thames water, from the clear water wells of eight Thames-derived supplies (mean of 201 samples)	26
Ditto ditto .. .. highest	202
Ditto ditto .. .. lowest	0
River Lea, unfiltered (mean of 26 samples) ..	1313
River Lea, from the East London Company's clear water well (mean of 26 samples) . ..	11

The water supply still remains in the same satisfactory condition as it was last month, when we said it was of exceptional microbic purity.

The number of analyses made in connection with former reports have reached a total per month of 182, but it will be observed that our present report deals with 208, or an additional number of 26 samples. Moreover, we have examined bacteriologically 422 samples, against an average of 292 samples in former months; showing an increase of 130. Our object in thus increasing the number of samples examined has been to meet the objection occasionally urged, that there were certain districts of London not served by special branch works or clear water wells from which we took the samples. By the inclusion of the additional samples taken from other districts named in the accompanying tables, we believe the whole of the water supply of the Metropolis is now substantially under examination as it is delivered into the mains of the respective Companies.

We are, Sir,
Your obedient Servants,
WILLIAM CROOKES.
JAMES DEWAR.

PROCEEDINGS OF SOCIETIES.

THE ROYAL SOCIETY CONVERSAZIONE.

June 21st, 1899.

A MOST brilliant and enjoyable *conversazione* was held at the Royal Society's Rooms, Burlington House, on Wednesday evening last. Owing to the unfortunate indisposition of Lord Lister, the guests and Fellows were received by Lord and Lady Kelvin. Among the many and varied exhibits the most interesting were:—

An apparatus shown by Mr. Mackenzie Davidson, M.B., by means of which Röntgen ray shadows could be seen in spectroscopic relief.

Experiments on the hissing of the electric arc were given by Mrs. Ayrton. On gradually increasing the current through an arc maintained between carbons at a fixed distance apart, a point is reached when the arc hisses, its appearance changes, and the electric pressure falls about 10 volts. The experiments show that this happens when the crater is too large to occupy the end only of the positive carbon, and therefore extends up its side. The crater, being no longer protected by carbon vapour from coming into direct contact with the air, now burns instead of volatilising, and it is this burning which causes hissing with its accompanying phenomena. This is proved (1) by excluding air from the arc, when experiment shows that the current can be increased, without producing hissing, to several times the value that would cause hissing in air; (2) by blowing air, or oxygen, down a tubed positive carbon, when hissing is found to take place even with quite a small current.

Experiments showing the manufacture of tubes from rock crystal in the oxy-hydrogen blowpipe flame by Mr W. A. Shenstone and Mr. W. T. Evans. Tubes of 1

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centimetre in diameter, composed of rock crystal, can now be made of considerable length at the rate of about 3 centimetres an hour.

Dr. Allan Macfadyen also showed some interesting cultures and microscopical slides of certain pathogenic bacteria, such as, for example, typhoid, cholera, plague, diphtheria, &c.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

NOTE.—All degrees of temperature are Centigrade unless otherwise expressed.

Comptes Rendus Hebdomadaires des Séances, de l'Académie des Sciences. Vol. cxxviii., No. 21, May 23, 1899.

New Compounds of Camphor with Aldehydes.—A. Haller.—The new compounds described in this paper are prepared by the action of piperonal and meta- and para-methoxybenzoic aldehydes on sodium camphor. These compounds of the aldehyde derivatives are easily reduced to alcoholic compounds. The reduction, instead of beginning on the group CO, as is the case with camphor, starts first on the non-saturated carbon group, C = C, then on the carbonyl group.

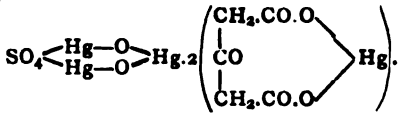
Action of Sulphuretted Hydrogen on Silicates.—P. Didier.—At a high temperature, hydrogen sulphide acts on the greater number of silicates and transforms them partially into sulphides. The author examines the cause of this reaction and the secondary reactions which accompany it for a certain number of minerals. The experiments are conducted in a porcelain tube at about 1400°, with a porcelain or carbon boat. In the greater number of experiments a small quantity of sulphuric acid is produced as a secondary reaction, which is found in the cold part of the tube. The displaced silica either is found free or else it forms silicates more acid than the original compound. The silica is not crystalline.

Di-isoamylacetic Acid.—H. Fournier.—The author prepared synthetically di-isoamylacetic acid by decomposing by heat di-isoamylmalonic acid, $(C_5H_{11})_2C(COOH)_2$. The latter acid was heated in an oil-bath to a temperature a little above its fusion-point. Carbonic acid began to be evolved at about 150°, and came off rapidly at 160°. The temperature was slowly raised to 175°, when the whole was cooled and the di-isoamylacetic acid extracted with alcohol. The acid thus prepared was in the form of white needle-shaped crystals, melting at 46—47°, insoluble in water, very soluble in ether, alcohol, carbon disulphide, and benzene. The acid was transformed into di-isoamylacetamide, $(C_5H_{11})_2CH—CONH_2$, by heating it with half its weight of phosphorus trichloride at 100° for half an hour. The resulting liquid is poured drop by drop into strong ammonia solution, and cooled by a freezing mixture. The crystals were washed with water and crystallised from alcohol.

Fluorine in Mineral Waters.—Charles Lepierre.—There exist certain mineral waters, very rare it is true, which are relatively very rich in fluorine. The most interesting example—perhaps unique in Europe—is that of the mineral waters of Gerez (North of Portugal). The author's analysis shows there to be 22 to 25 m.grms. of alkaline fluoride (probably sodium) per litre, which amounts to 10 to 12 m.grms. of combined fluorine. It is enough to evaporate half a litre of Gerez water in a platinum dish to discover positively the existence of fluorides in the residue. The analytical detection of fluorine in the waters can be made—(1) By the ordinary method of heating the residue from the water with sulphuric acid and showing the corrosion of glass; (2) by Lannes' or Carnot's method; (3) if silica is present, by the formation of SiF_4; (4) by the formation of crystals of fluosilicate of sodium, of which the little hexagonal prisms are characteristic. This last reaction is very sensitive.

Bulletin des Travaux de la Société de Pharmacie de Bordeaux. April, 1899.

Acetone Dicarbonic Acid: a Product of the Manganic Oxidation of Citric Acid.—G. Denigès.—The author found that acetone-dicarbonic acid gave with mercuric bisulphate a compound corresponding to the formula—



This compound was obtained by boiling 100 c.c. of the sulphate of mercury reagent (prepared by dissolving 5 grms. of red or yellow mercuric oxide in a warm mixture of 20 c.c. of sulphuric acid and 100 c.c. of water) and, *immediately on removing from the fire*, adding a *cold* solution of 1 grm. of acetone-dicarbonic acid in 125 c.c. of water. The abundant white precipitate is allowed to settle, washed by decantation, and filtered; it is then dried, first on porous plates, then over concentrated sulphuric acid. Analysis gives:—

	Found.	Calculated for $SO_4Hg.2HgO.2(C_6H_4O_5Hg)$.
Hg (per cent)	70·25	70·62
SO_4H_2 ,, ...	6·97	6·92
C ,, ...	8·12	8·48
H ,, ...	0·65	0·56

It is a white substance, soluble in hydrochloric acid, insoluble in water. The author shows that it is identical with the compound given by sulphate of mercury with the products of the manganic oxidation of citric acid.

On a very Sensitive Reaction of Acetone-dicarbonic Acid.—G. Denigès.—To detect the presence of very small quantities of this acid, we add to the solution under examination one-tenth of its volume of the mercuric reagent and stir well. The reaction is never instantaneous, but after a short interval—perhaps even some minutes, if only a few m.grms. per litre are present—a white cloudiness is suddenly formed, quickly followed by a precipitate if the proportion of acid present reaches some centigrms. per cent. With solutions containing at least 5 centigrms. of acid per litre, the characteristic cloudiness is obtained before the liquid boils, and, in the case of very concentrated solutions, almost immediately on mixing. With only 2 m.grms. per litre, the sudden cloudiness only appears fifteen or twenty minutes after the boiling-point has been reached and the tube withdrawn from the flame. The approximate estimation of acetone-dicarbonic acid can be easily made by chronometric means, by adding 0·5 c.c. of the mercuric reagent to 5 c.c. of the solution under examination and noting the exact number of seconds before the cloudiness appears, and referring to a table here given.

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THE CHEMICAL NEWS.

Vol. LXXIX., No. 2066.

ON THE COMPARATIVE EFFICIENCY AS CONDENSATION NUCLEI OF POSITIVELY AND NEGATIVELY CHARGED IONS.*

By C. T. R. WILSON, M.A.

The experiments described in this paper were undertaken with the object of throwing some light upon what appeared to be fundamental questions in connection with the electrical effects of precipitation. It was hoped in this way to make some advance towards an understanding of the relation between rain and atmospheric electricity.

It was pointed out by Professor J. J. Thomson (*Phil. Mag.*, December, 1898) that if positive and negative ions differed in their power of condensing water around them, drops might be formed upon one set of ions only, and separation of positive and negative electricity would then take place by the falling of the drops, the work required for the production of the electric field being due to gravity.

To make this process worthy of consideration as a possible source of atmospheric electricity, it would be necessary to show reason for believing (1) that atmospheric air in the regions in which rain is formed is likely to contain free ions, (2) that positively and negatively charged ions differ in their efficiency as condensation nuclei.

It is mainly with the second of these questions that this paper deals. The result of this part of the investigation was to prove that water condenses much more readily on negative than on positive ions. The experiments consisted in measurements of the expansion required to cause condensation in the form of drops in air initially saturated and containing ions, alternately nearly all positive and nearly all negative. The ratio of the final to the initial volume being indicated by v_2/v_1, then to cause water to condense on negatively charged ions, the supersaturation must reach the limit corresponding to the expansion, $v_2/v_1 = 1{\cdot}25$ (approximately a fourfold supersaturation). To make water condense on positively charged ions, the supersaturation must reach the much higher limit, corresponding to the expansion $v_2/v_1 = 1{\cdot}31$ (the supersaturation being then nearly sixfold).

We see, then, that if ions ever act as condensation nuclei in the atmosphere, it must be mainly or solely the negative ones which do so, and thus a preponderance of negative electricity will be carried down by precipitation to the earth's surface.

Incidentally it was proved that the difference between the effects as condensation nuclei of the positively and negatively charged ions is not to be explained by supposing that the charge carried by the negative ions is, say, twice as great as that carried by the positive ions, for equal numbers of positive and negative ions are produced by the ionisation of the neutral gas.

Attempts were now made to find an answer to the first question suggested above—Is there any evidence that ions are likely to be present under normal conditions in the atmosphere?

Former experiments furnished a certain amount of evidence in favour of an affirmative answer.

When moist dust-free air is allowed to expand suddenly a rain-like condensation always takes place if the maximum supersaturation exceeds a certain limit. This limit is identical with that required to make water condense on ions; the identity is in fact so exact as to furnish what is at first sight almost convincing evidence that ordinary moist air is always to a very slight extent ionised. The number of these nuclei is too small to make the absence of sensible electrical conductivity in air under ordinary conditions inconsistent with the view that they are ions.

All attempts, however, to remove these nuclei, by applying a strong electric field such as would have removed ordinary ions almost as fast as they were produced, have failed, even when a differential apparatus was used such as would have made manifest even a slight diminution in the number of the nuclei by the action of the field. The same is true of the similar nuclei produced by the action of weak ultra-violet light on moist air.

Such nuclei, therefore, in spite of their identity as condensation nuclei with the ions, cannot be regarded as free ions, unless we suppose the ionisation to be developed by the process of producing the supersaturation. This question requires further investigation.

* Abstract of a Paper read before the Royal Society, June 15, 1899.

A COMPARISON OF PLATINUM AND GAS THERMOMETERS, INCLUDING A DETERMINATION OF THE BOILING-POINT OF SULPHUR ON THE NITROGEN SCALE:

An Account of Experiments made in the Laboratory of the Bureau International des Poids et Mesures, at Sevres.*

By Drs. J. A. HARKER and P. CHAPPUIS.

In 1886 Professor Callendar drew attention to the method of measuring temperature, based on the determination of the electrical resistance of a platinum wire. He showed that the method was capable of a very general application, and that the platinum resistance thermometer was an instrument giving consistent and accurate results over a very wide temperature range.

Callendar pointed out that if R_0 denote the resistance of the spiral of a particular platinum thermometer at 0°, and R_1 its resistance at 100°, we may establish for the particular wire a temperature scale, which we may call *the scale of platinum temperatures*, such that if R be the resistance at any temperature T°, this temperature on the platinum scale will be—

$$\frac{R}{R_1 - R_0} \times 100 \text{ degrees.}$$

For this quantity Callendar employs the symbol pt, its value depending on the sample of platinum chosen.

In order to reduce to the standard scale of temperature the indications of any platinum thermometer, it is necessary to know the law connecting T and pt. These are, of course, identical at 0° and 100°, but the determination of the curve expressing the relationship between them is a matter for experiment.

The work of Callendar had established for a particular sample of platinum the relation—

$$d = T - pt = \delta\left[\left(\frac{T}{100}\right)^2 - \frac{T}{100}\right]$$

over the range 0° to 600°, T being measured on the constant pressure air scale.

Later experiments by Callendar and Griffiths showed that this relation holds for platinum wires generally, provided they are not very impure. They propose that the value of δ, the constant employed in the formula, should be determined by taking the resistance of the thermometer in the vapour of sulphur. A new determination of this point on the air scale made by them gave 444·53° as the boiling-point under 760 m.m. pressure.

* Abstract of a Paper read before the Royal Society, June 15, 1899.

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The present paper is the outcome of the co-operation of the Kew Observatory Committee and the authorities of the International Bureau of Weights and Measures at Sèvres, for the purpose of carrying out a comparison of some platinum thermometers with the recognised international standards.

A new resistance-box, designed for this work, and special platinum thermometers, together with the other accessories needed, were constructed for the Kew Committee, and, after their working had been tested at Kew, were set up at the laboratory at Sèvres, in August, 1897. The comparisons executed between these instruments and the standards of the Bureau may be divided into several groups. The first group of experiments covers the range −23° to 80°, and consists of direct comparisons between each platinum thermometer and the primary mercury standards of the Bureau. Above 80° the mercury thermometers were replaced by a gas-thermometer, constructed for measurements up to high temperatures. The comparisons between 80° and 200° were made in a vertical bath of stirred oil, heated by different liquids boiling under varying pressures. For work above 200° a bath of mixed nitrates of potash and soda was substituted for the oil tank. In this bath comparisons of the two principal platinum thermometers with the gas-thermometer were made up to 460°; and with a third thermometer, which was provided with a porcelain tube, we were able to go up to 590°. Comparisons of the platinum and gas-scales were carried out at over 150 different points, each comparison consisting of either ten or twenty readings of the different instruments.

By the intermediary of the platinum thermometers a determination of the boiling-point of sulphur on the nitrogen scale was also made. The mean of three very concordant sets of determinations with the different thermometers gave 445·27° as the boiling-point on the scale of the constant volume nitrogen thermometer, a value differing only 0·7° from that found by Callendar and Griffiths for the same temperature expressed on the constant pressure air scale.

If for the reduction of the platinum temperatures in our comparisons we adopt the parabolic formula, and the value of δ obtained by assuming our new number for the sulphur-point, we find that below 100° the differences between the observed values on the nitrogen scale and those deduced from the platinum thermometer are exceedingly small, and that even at the highest temperatures the differences only amount to a few tenths of a degree.

Full details as to the instruments employed and the methods adopted are given in the paper.

ON SOME PHOTOGRAPHIC PHENOMENA CONNECTED WITH THE COLSON-RUSSELL EFFECT.

By J. H. VINCENT, D.Sc. (Lond.), A.R.C.Sc.

Introduction.

Colson, who has for several years been publishing papers on the effects of various agents on a photographic plate, first found that heat in presence of moisture from paper, &c., was able to so affect a photographic plate as to cause a darkening of the sensitive surface when the plate was treated with a developer (*Comptes Rendus*, Jan., 1896, cxxii., 598—600). Colson subsequently found that the air in the neighbourhood of some bright metals possessed a similar property (*Comptes Rendus*, Jan., 1896, cxxiii., 49—51). This he attributed to the action of the vapours of the metals themselves.

Russell discovered both these effects quite independently a little later, and in a series of papers (Chemical News, lxxv., 302; 1898, lxxvii., 167; *Proc. Roy. Soc.*, xiii., 102; lxiv., 409) has shown that both classes of effect are probably due to the same active agent. This agent is, in his opinion, hydrogen peroxide, and he has obtained chemical tests for the presence of this body in all cases in which the plate has been darkened by the emanations under discussion. The chemical recognition of hydrogen peroxide is a matter of great difficulty and uncertainty, and the probability of the truth of Russell's theory rests more securely on the perfect analogy which he has shown to exist between the behaviour of the vapours from active bodies and that of hydrogen peroxide. The completeness with which this similarity in properties is exhibited is remarkable, and can hardly be capable of any other interpretation than that of the identity of the active agents.

It must be borne in mind, however, that another explanation of the photographic activity of metals like zinc has been put forward by von Lengyel (*Wied. Ann.*, 1898, lxvi., [5], pp. 1162-1170), who looks upon hydrogen as the active agent. According to this author, hydrogen has an effect on a photographic plate similar to that of light, producing a modification of silver bromide which is reduced by an ordinary developer. Russell, however, states in his first paper that in an atmosphere of hydrogen the action takes place as in ordinary air. This means that the effect of the hydrogen itself was so slight as not to be noticed by Russell, in comparison with the effect of the active bodies he was investigating.

The work of Russell shows that the dry plate furnishes a means to distinguish between hydrogen peroxide and ozone, as the latter does not affect the film. But in making use of this test the action of ozone upon any substance in the neighbourhood of the plate must be considered. It is the object of this paper to show that some bodies, which, although perfectly inactive previously, become strongly active when treated with even small quantities of ozone.

Experiments with Indiarubber.

Indiarubber, as Russell has proved, is an inactive substance. That is to say, it may be put in contact with a photographic dry plate for a week or so without exerting any effect on the plate capable of causing darkening on development. But if ozonised air be allowed to come into contact with the rubber for only a short time, it becomes so active as to give a picture in a few minutes. The effect may be heightened by passing the ozonised air over the indiarubber in a gentle stream; in this way, five minutes ozonising and five minutes exposure of the plate are quite sufficient to give a dark picture when Ilford special rapid plates are used.

The mode of experimenting may be varied as follows:—A box of lead was taken and a sheet of rubber stretched over the top; this rubber was held in position conveniently by the lid of the box, also of lead. Two tubes of the same metal are provided for the entrance and exit of air, and these tubes have their openings beneath the rubber diaphragm. The tubes are bent so as to render the box light tight (Fig. 1). If now a plate be put into the box with its sensitive film facing the surface of the rubber, and a coin or piece of glass or quartz be placed upon it, no picture is obtained, by passing ordinary air through the apparatus; neither is any picture obtained if ozonised air be used and the rubber be absent. If, however, ozonised air and rubber be used, a picture is easily obtained in a few minutes. The effect is not one of light, since the quartz and glass appear equally opaque to the effect as the metals.

The rubber, on testing, is found to be photographically active either before or after removal from the box. The activity persists for some days afterwards, even when the time during which ozonised air has had access to it has only been a few minutes. The action of ozone on rubber is well known as regards its physical effects. If rubber tubing be used to convey ozonised air, it rapidly becomes so changed that, on slightly stretching it, it breaks up in transverse rings. The action is well shown on photographs

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of rubber sheeting obtained by contact in the dark. If the ozonisation has been continued so long as to have caused the rubber to break, the broken edges are beautifully distinct on the photograph. This indicates that the activity of the rubber arises from some product of the action of ozone on the rubber itself, as distinct from any action that may occur between the ozone and the water or other bodies present.

The effect of ozonised rubber is probably due to the formation of hydrogen peroxide. Indiarubber yields on distillation, at moderate temperatures, bodies such as isoprene, more or less allied to the terpenes. Thus it seems possible that rubber itself consists largely of bodies chemically related to the terpenes. The latter are well known to yield hydrogen peroxide on oxidation, and Russell has shown that all the terpenes are photographically active.

Sensitiveness of this Test for Ozone.

The amount of ozone necessary to obtain these pictures seems to be very small; for if the positive or negative brush discharge from a small Wimshurst machine be allowed to play on a disc of metal with a central aperture leading through one of the lead tubes to the box in the apparatus above described, the pictures can be obtained in an hour, even without drawing the ozonised air over the rubber. The ozone necessary reaches the rubber by diffusion only.

Tests for H_2O_2.

A glass tube, 2 feet long and an inch wide, was loosely packed with shreds of pure rubber. Ozonised oxygen, after passing through the tube, was photographically active. The rubber was then washed with water, and the latter gave the tests for H_2O_2 with chromic acid and titanic acid. This water was also exceedingly active photographically; a plate placed a quarter of an inch from its surface gave a good picture in ten minutes, while painting the liquid on to the plate produced solarisation almost immediately.

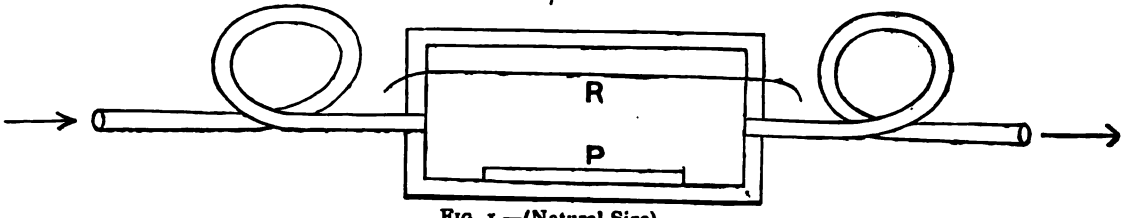

Fig. 1.—(Natural Size).

R, Indiarubber. P, Plate.

Mr. Bryan was good enough to test some rubber sheets in his apparatus for investigating the effect of bodies on the contact difference of potential between two metals. He found that rubber itself had no influence, while ozonised rubber and rubber exposed to the vapour of hydrogen peroxide had an effect in the same sense. This result is not properly to be interpreted by remarking that ozone and hydrogen peroxide both affect the rubber similarly, since hydrogen peroxide apparently has no chemical action on rubber. It rather shows that hydrogen peroxide is a product of ozonisation of rubber.

Transfer Pictures.

If a plate, after being subjected to the influence of the ozonised rubber, be placed upon another plate before development, then, after the films have been in contact some time, the picture may be developed on both the plates. Thus these pictures can not only be taken, but also in a sense printed, in the dark. Prof. J. J. Thomson informs me that Russell has also obtained such pictures; a similar phenomenon is mentioned in Russell's papers, in which the first photographic film is replaced by a non-active body capable of transmitting the effect. This capacity of printing transfers is of use in satisfying the experimenter that any particular effect is not due to radiation of any type. Such transfer pictures have been said to be capable of production by light. But the universal practice of photographers is to store exposed plates film to film before development. No such phenomenon ever occurs as the one exposed plate affecting the other. Another reason for thinking that any such effect is absent is found in the total lack of any accumulative continuing action of light on a photographic dry plate. Experiments to obtain transfers with dry plates and daylight were carried out, both with normal exposures and also with exposures producing solarisation, but not the slightest effect could be obtained. These remarks do not apply to the bichromate processes in which continuing action does occur (Vogel, "The Chemistry of Light and Photography," 1875, p. 242), as is well known, and transfer pictures by contact in the dark can be obtained (*Brit. Journ. Phot. Almanack*, 1899, p. 822).

The active agent from ozonised rubber passes through paper, gelatin, tracing paper, &c., in the same way as with Russell photographs; and bodies like the metals, glass, and quartz are opaque to it.

Experiments with other Bodies.

The common varieties of gutta-percha also become fairly active on ozonising; but pure gutta-percha becomes only slightly active, so as to require ozonised air to be in contact with the sheet for a quarter of an hour, and a subsequent exposure of the plate for half an hour, in order to obtain a picture capable of development.

It is interesting to note that camphor also becomes active by treatment with ozone. In experimenting with bodies other than rubber it is best to use oxygen instead of air, as this is an economy of time. On ozonising camphor for ten minutes, it becomes active enough to give a good picture with a quarter of an hour exposure. As Russell has previously shown, camphor, indiarubber, and gutta-percha are ordinarily quite inactive, though capable of transmitting the active agent.

Those other bodies (including cork, vulcanite, and gelatin) which have been tested with ozone are either inactive or else the effect is much less than in the above cases.

Cavendish Laboratory, Cambridge.

SODIUM ALUMINATE AS A MEANS FOR THE REMOVAL OF LIME AND SUSPENDED MATTER FROM WATER FOR USE IN BOILERS.*

By CHARLES F. MABERY and EDWIN B. BALTZLEY.

Throughout the section of country including Northern Pennsylvania, Ohio, and farther west, in districts removed from the lake or the large rivers, the only sources of water in seasons of drought are deep wells. Since the water from these wells contains large quantities of lime

* Contributions from the Chemical Laboratory of the Case School of Applied Science. From the *Journal of the American Chemical Society*, xxi., No 1. (The work described in this paper formed the subject of a thesis for the degree of Bachelor of Science).

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salts, there are serious difficulties in the way of procuring water suitable for use in steam boilers, especially in locomotive boilers. Even such water as that from Lake Erie or the rivers, deposit scale to such an extent as to occasion extreme inconvenience. In stationary boilers, the deposition of scale may be avoided at least in part by using some one of the many so-called scale preventatives, if the boiler is in charge of an intelligent engineer.

The inconvenience of boiler scale, the additional cost in fuel, the injury to the boiler, and the danger are features of this question familiar to all who have charge of boilers. The large masses of scale withdrawn from boilers in which hard or turbid water is used, are not surprising when the great quantities of water evaporated in boilers under high pressures are taken into consideration.

The wide variations in the composition of boiler scale are dependent on the differences in the water used. The manner of running the boiler has much to do with the hardness of the scale and the rapidity of its formation. The chief causes of the formation of scale are the calcium carbonate and sulphate and magnesium carbonate contained in solution, and the solid matter held in suspension, both inorganic and organic. All these points must be borne in mind if unpurified water is to be used in a boiler. There has been for some time a feeling on the part of engineers that the only satisfactory method for the prevention of boiler scale is the use of purified water, and many attempts have been made, with more or less success, toward purification of the water before it enters the boiler. The means that have been tried include sedimentation, precipitation by sodium carbonate, sodium hydroxide, slaked lime either alone or in combination. Evidently successful purification depends on removing completely the suspended matter as well as the precipitation of the lime and magnesia. In thinking of what combination should most effectually and economically accomplish these results, in any hard or turbid water, it occurred to one of us (Mabery), that sodium aluminate should fulfil the conditions demanded, and in trying this reagent we find that it meets all requirements.

The general method includes the preparation of sodium aluminate in solution. This may be done in any suitable tank or reservoir, by adding sodium hydroxide in the proper amount to a solution of aluminum sulphate of known strength, and adding to the water a definite amount (the quantity depending on the composition of the water to be purified), agitating thoroughly, and allowing the mixture to stand some time, perhaps twelve to twenty-four hours. The method is based on the following reactions:—

For the formation of sodium aluminate—

$$Al_2(SO_4)_3+8NaOH=Al_2O_4Na_2+3Na_2SO_4+4H_2O.$$

In the precipitation—

$$CaH_2(CO_3)_2+Al_2O_4Na_2+2H_2O=$$
$$=CaCO_3+2AlO_3H_3+Na_2CO_3.$$
$$CaSO_4+Na_2CO_3=CaCO_3+Na_2SO_4.$$

Similar reactions evidently take place with magnesium carbonate or sulphate. No doubt sodium aluminate can be made much more cheaply by fusing a tolerably pure clay with soda-ash. Doubtless it may also be obtained cheaply as one of the products in the preparation of soda-ash from cryolite.

Numerous experiments were made with different proportions of sodium aluminate; the best results were obtained by using from one-half the calculated proportions to the calculated proportions of aluminum sulphate, depending on the composition of the water. With proper proportions of aluminate, aluminum hydroxide was completely precipitated on standing. Experiments on different waters with one-fourth the calculated proportion of aluminate showed that this amount was not sufficient to precipitate the lime sufficiently. In applying this method its effect was studied on waters containing different amounts of carbonate and sulphate, as well as on waters with a great variation in turbidity, from the slightly turbid lake water, to specimens thick and muddy. In every instance after standing from twelve to twenty-four hours, the water became perfectly clear. The extent to which lime and magnesia were removed is shown by results obtained in the following waters:—

Very hard water from well in Ohio—

Calcium sulphate	259·0
Calcium carbonate	146·0
Magnesium carbonate	177·3

About 85 per cent of the amount of aluminate required to precipitate all the lime and magnesia was added, air was blown through the solution for a few minutes and the mixture allowed to stand twenty-four hours. Analysis then showed that 88 per cent of the lime had been removed and 95·6 per cent of the magnesia. In another determination the theoretical amount of aluminate was added and the solution treated as before. Analysis showed that 98·1 per cent of the lime had been removed and 97·4 per cent of the magnesia.

The next water tried was the Massillon city water, containing—

Calcium sulphate	99·12
Calcium carbonate	113·2
Magnesium carbonate	131·1

After treatment with the theoretical amount of sodium aluminate the total lime removed was equivalent to 98·8 per cent, and that of magnesia 98·0 per cent.

In another experiment, using one-half the theoretical amount, the lime removed was 83·5 per cent, and that of the magnesia 90·6 per cent.

The next water tried was a very turbid sample from the Cuyahoga river. This water was very muddy and did not settle on long standing. It is used in boilers. A clear sample of this water showed the following composition:—

Calcium sulphate	68·0
Calcium carbonate	14·14
Magnesium carbonate	21·3

Treatment with the theoretical amount of aluminate gave unsatisfactory results.

With twice the theoretical amount, the lime remaining was 88·3 per cent, and the magnesia 84·5 per cent. The aluminate is especially serviceable in such waters as this in removing completely the turbidity.

Although the water of Lake Erie does not contain a large proportion of solid matter, it forms scale quite rapidly unless some means are taken to prevent it. Analysis of a sample collected April 28, 1898, gave—

Calcium carbonate	53 63
Calcium sulphate	32·61
Magnesium carbonate	21·53

Analysis, after treatment with theoretical aluminate, gave 97·6 per cent lime, and 93·2 per cent magnesia removed, after standing thirty-six hours. With one-half the theoretical amount standing forty-eight hours 98·3 per cent of the lime was removed and 90 per cent of the magnesia. With one-fourth the theoretical amount 83 per cent of lime was removed and 60 per cent of the magnesia.

From a very muddy brook water containing much suspended matter, with—

Calcium sulphate	8·1
Calcium carbonate	120·0
Magnesium carbonate	23·0

after standing forty-eight hours, the theoretical amount of aluminate removed 96 per cent of lime and 96 per cent of magnesia. One-half the theoretical amount removed 94·6 per cent lime, and 94·4 per cent magnesia.

In treating the water from a well in Ashtabula, O., containing—

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Calcium sulphate	96
Magnesium sulphate	39

the theoretical amount of aluminate removed 98 3 per cent of the lime and 96 per cent of the magnesia.

A well in Glenville, O., containing—

Calcium carbonate	99
Calcium sulphate	36
Magnesium carbonate	23

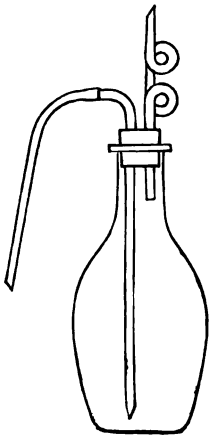
after treatment with theoretical aluminate showed that 98·1 per cent of the lime had been removed and 95 per cent of the magnesia.

To test still further the efficiency of the aluminate, experiments were made with sodium hydroxide alone, using various proportions, but the removal of lime was not much more than half the quantity taken out by aluminate, and the magnesia was not affected. An important effect of alumina is to remove suspended matter, which it does rapidly and completely.

AN APPARATUS TO FACILITATE HYDROGEN SULPHIDE PRECIPITATIONS.*

By RICHARD K. MEADE.

The piece of apparatus described below has been in use here for the past term by the students of my class in qualitative analysis and answers fully the purpose for which it was designed: to hasten the precipitation of the copper-arsenic group by hydrogen sulphide. It consists of an ordinary flask or gas bottle of any suitable form and capacity, provided with a closely-fitting two-hole rubber stopper. A piece of glass tubing bent at right angles passes through one hole to the bottom of the flask, serving as an inlet for the gas. This is connected with the hydrogen sulphide generator by a half or



three quarters of a yard of light rubber tubing. A piece of glass tubing bent in the gas flame to the form shown in the cut passes through the other hole and serves as an outlet for the gas.

The solution to be precipitated is poured into the flask, this in turn corked up, and the apparatus stood in the hood. The gas is now passed into the solution and the flask violently shaken by hand. The bends in the exit tube keep any of the solution from being thrown out of the flask. The churning up of the solution with the hydrogen sulphide gas quickly throws out of solutions the metals of the copper-arsenic group.

The young men tell me that not only is the time necessary for complete precipitation greatly shortened, but the sulphides are obtained in a form more easily filtered and washed, by the use of this apparatus.

THE MANUFACTURE OF BARIUM CHLORIDE AND PERMANENT WHITE.

By K. W. JURISCH.

Some time ago, at a chemical works in the North of France, the following operations were carried on:—

Witherite was dissolved in hydrochloric acid and the solution of barium chloride, freed from the greater part of the iron, was evaporated down, or else treated with sulphuric acid, with the object of producing permanent white.

The witherite employed had the following composition:—

$BaCO_3$..	85·98	88·77	77·61
$CaCO_3$..	0 68	2·75	3·91
Fe_2O_3	0·1112	1·17	11·30 (insoluble)
Al_2O_3		7·24	3·58 (insoluble)
SiO_2			1·06
Residue	11·97	—	1·83
Water	0·95	0·25	0·63
	99·6912	100·18	99·92

The crystallised barium chloride contained:—

$BaCl_2$	81·58
$CaCl_2$	1·90
Water	16·22
	99·70

The pasty permanent white as it left the filter-press contained approximately:—

Water	19·75
$BaSO_4$	80·25
$CaSO_4$	Traces

At the present time attempts are being made to replace the witherite—of which the price is high—by heavy spar, which can be obtained at a cheap rate.—*Zeitschrift für Angewandte Chemie*, No. 9, p. 198, 1898.

ON SOME COMPOUNDS OF TITANIC ACID WITH SULPHURIC ACID.

By M. BLONDEL.

I. *Compounds formed with Concentrated Sulphuric Acid.*

Mertz has shown that a solution of titanic acid in sulphuric acid, evaporated rapidly, leaves a gummy mass the composition of which agrees with the formula $TiO_2.SO_3$.

Under slightly different conditions, we have succeeded in preparing two crystalline compounds of titanic acid with sulphuric acid.

The sulphuric solution of titanic acid, heated in a closed vessel, changes in fact at 120° into a mass of crystals having a silky lustre, soluble in water slightly acidulated with hydrochloric acid, having the composition $2TiO_2.3SO_3.3H_2O$.

If we gradually increase the temperature to 225°, the deposit changes into rhombohedric crystals, slowly decomposable by water into basic sulphate and sulphuric acid and having for their composition the formula $TiO_2.SO_3$; under the prolonged action of a temperature

* Contributio from the Chemical Laboratory of Lafayette College. From the *Journal of the American Chemical Society*, xxi No 5.

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of 225° the whole of the titanic acid leaves the solution and passes into the crystals.

When we attempt to dissolve rutile in concentrated sulphuric acid, and if we allow the temperature to go above 225°, the mineral becomes coated with a layer of sulphate which protects it from complete solution. This will explain the difficulty experienced in dissolving even porphyrised rutile in sulphuric acid. H. Rose recommends diluting the acid with its own volume of water, which diminishes the energy of the acid, but stops the rise of temperature, and consequently the formation of the protective coating. We can with advantage make use of concentrated acid if we carry out the operation in an oven in which the temperature is not allowed to exceed 200°.

II. *Compounds formed in Dilute Sulphuric Acid.*

1. A solution of no matter what proportion of titanic acid in concentrated sulphuric acid, diluted with its own volume of water precipitates, at all temperatures starting from 100°, long needles easily soluble in water, having a composition of $TiO_2.SO_3.2H_2O$.

2. A solution of 0·5 part of titanic acid in 1·0 part of concentrated sulphuric acid, diluted with 1·5 parts of its weight of water, precipitates sulphates of titanic acid of variable composition according to the temperature; at a temperature of 100° the formula will be $2TiO_2.SO_3 + Aq.$; at a temperature of 130° the formula is $7TiO_2.2SO_3 + Aq.$

3. A solution of any proportion of titanic acid in concentrated sulphuric acid, moderately diluted with water (1 to 5), deposits sulphates up to 175°, and at 175° anhydrous crystallised titanic acid.

4. A solution of any proportion of titanic acid in concentrated sulphuric acid, strongly diluted (1 to 10) with water precipitates at the ordinary temperature, though slowly, the well defined compound $5TiO_2.SO_3.5H_2O$; at 100° the titanic solution retains, as is well known, traces of sulphuric acid, which cannot be removed even after prolonged washings.

5. Furthermore, a sulphuric solution of titanic acid, first diluted with water and then treated with a small quantity of ammonia, deposits on evaporation *in vacuo* crystals belonging to the cubical system and showing tetrahedric hemihedra. They have for formula $2TiO_2.2SO_3.NH_4O.3H_2O$. These crystals are slowly decomposed by water and effloresce when exposed to the air.—*Bull. Soc. Chim.*, Series 3, vol. xxi., No. 6.

ON THE CHEMICAL PROPERTIES OF IODOFORM AND ITS DETECTION IN AQUEOUS SOLUTIONS.

By Dr. L. V. STUBENRAUCH.

When we mix a certain quantity of iodoform with a dilute solution of argentic nitrate (at about 1 per cent) at the ordinary temperature no change is observed; but on heating there is a disengagement of carbonic oxide and the formation of a stiff cheese-like precipitate of yellow iodide of silver—

$$CHI_3 + 3AgNO_3 + H_2O = CO + 3AgI + 3NO_3H.$$

Solid nitrate of silver attacks iodoform in a still more energetic manner and even in the cold. By grinding up these two substances together we notice that heavy fumes of nitric oxide and of iodine are given off, together with the formation of argentic iodide and probably also of carbonic oxide.

We know from Daccomo's work on the subject (*Gass. Chim. Ital.*, 1871, No. 6, p. 247) that solid iodoform undergoes decomposition under the influence of atmospheric air and of oxygen, while carbonic acid and nitrogen have no action on this body.

Iodoform, when suspended in water, is decomposed by the action of light, the more energetically and rapidly as the intensity of the light is greater. The products of this decomposition are free iodine and hydriodic acid, which both enter into solution, communicating a more or less pronounced yellow colour.

The principal tests which can be used for the detection of iodoform are the following:—

1. The odour, which may, however, be hidden by that of other substances.

2. The microscopic examination of the crystals of iodoform; alcoholic and ethereal solutions give well defined hexagonal tablets. Such an examination may, however, give rise to errors.

3. The action of light, which, as has just been said, decomposes iodoform, colouring its solution yellow. This test is not to be depended upon unless we can be sure of the absence of free hydriodic acid and of alkaline iodides.

4. The phenic reagent of Reiner and Tiemann modified by Lustgarten. We add one or two drops of an alcoholic solution of iodoform to a small quantity of the reagent (20 parts of phenic acid, 40 parts of caustic soda, 70 parts of water) and heat gently. Salicylic aldehyde is formed, and at the same time, owing to a secondary reaction, a red precipitate is formed, which, dissolving in the dilute alcohol, gives it a carmine-red colour. The presence of potassic iodide has no influence, but the experiment does not always succeed.

Fuming nitric acid, used in very small quantity, is an excellent reagent for detecting iodoform in aqueous solutions.

Thus, by adding *one drop* of fuming nitric acid to 3 or 4 c.c. to an aqueous solution of potassic iodide, hydriodic acid or an easily decomposed organic body containing iodine, and then a little starch paste, an intensely blue colouration appears, while iodoform treated in exactly the same manner remains unchanged and does not colour starch. On the other hand, iodoform suspended in water, reduced while hot by powdered zinc and 1 drop of glacial acetic acid, gives a filtrate which gives the blue colour to starch in the presence of fuming nitric acid.

If therefore a solution colours starch blue after having been treated with 1 drop of fuming nitric acid, there is reason to believe that potassic iodide, free hydriodic acid, or a soluble unstable organic compound of iodine is present; but when the acid does not produce iodide of starch, if the blue colour does not show itself until after the reduction by powdered zinc and glacial acetic acid, the presence of iodoform is confirmed.

This reaction is not applicable when the aqueous solution contains besides iodoform, a more or less large proportion of an alkaline iodide, hydriodic acid, or an easily decomposed organic compound of iodine.

The presence of albumen in a moderate amount interferes with the detection of iodoform in aqueous solution by this method.

It is preferable to use a mixture of nitrite of soda and sulphuric acid, instead of fuming nitric acid.—*Zeit. f. Untersuchung der Nahrungs und Genussmittel*, 1898, p. 737.

ON THE DECOMPOSITION OF CARBONIC OXIDE IN THE PRESENCE OF METALLIC OXIDES.

By O. BOUDOUARD.

H. Sainte-Claire Deville has shown that carbonic oxide dissociates, giving carbonic acid and carbon; he has also established the apparently paradoxical proposition that carbonic oxide, in the presence of red-hot carbon, becomes partially transformed into carbonic acid and carbon (*Comptes Rendus*, vol. lix., p. 873; and vol. lx., p. 317).

Iron, and especially finely divided iron, seems to favour this decomposition. Stammer was the first to notice

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(*Ann. de Poggendorff.*, 1851, vol. lxxxi., p. 136), that in passing carbonic oxide over iron, below the softening point of glass, there was besides the iron reduced, a considerable quantity of voluminous carbon uniformly impregnated with iron.

Caron (*Comptes Rendus*, vol. lii., p. 1190) and Lowthian Bell (*Journ. Chem. Soc.*, June, 1869; *Journ. Iron and Steel Inst*, 1871, vol. i., p. 85) have made similar observations, but, contrary to the results of Deville and Gmelin, Lowthian Bell concluded that heat alone does not dissociate carbonic oxide; Deville must have precipitated the carbon of the carbonic oxide at a point where reoxidation was not possible. For this phenomenon to take place, it is necessary to operate in the presence of metallic oxides; the oxides of iron, nickel, and cobalt give the best results.

With the other metallic oxides, operating for longer or shorter periods, at temperatures varying from the melting point of zinc to red-heat Lowthian Bell observed the following facts:—

1. With titanium, the metal appears to be impregnated with carbon.

2. With copper and lead there was no deposit of carbon, but reduction of the oxide to the state of metal.

3. With manganese, no deposit of carbon and reduction to the state of protoxide.

4. With zinc, chromium, tin, and silicon, nothing.

MM. Schlagdenhauffen and Pagel seem to believe, on the contrary, that the deposition of carbon takes place with all the oxides, in particular with oxide of lead (*Comptes Rendus*, vol. cxxviii., p. 311). Now, if we refer to the experiments 387 and 388 of Lowthian Bell, which were made with oxide of lead obtained by the calcination of the nitrate, either at the temperature of fusing zinc, or at a red-heat, we note that no deposit of carbon was observed. The action of carbonic oxide on the oxides of copper and lead, which is so simple since there is only one phenomenon of reduction, is much more complex with the oxides of iron, nickel, and cobalt.

Deville has further noticed that by submitting a bundle of pianoforte-wire placed in a porcelain tube heated for a portion of its length only, so that the middle part is at 1300° and the extremities at 400°, to a current of carbonic oxide, the latter parts only become coated with carbon, the part heated to redness is transformed into steel.

Grüner (*Comptes Rendus*, vol. lxxiii., p. 28; vol. lxxiv., p. 226), has offered the opinion that the ferruginous carbon obtained by the reduction of the oxide of iron by the carbonic oxide always contains a certain proportion of undecomposed oxide of iron, and that pure carbonic oxide cannot deposit carbon on the pure iron. If this is really the fact it should be attributed to the previous presence of carbonic acid in the carbonic oxide, or of sesquioxide of iron in the iron.

According to M. Berthelot, who has studied the action of heat on carbonic oxide (*Ann. Chim. Phys.*, Series 6, vol. xxiv., p. 126; *Comptes Rendus*, vol. cxii., p. 394), the appearance even of carbonic acid in notable quantity, either at a red heat or at 550°, whether with the deposition or not of this element, leaves no doubt as to the mechanism of the decomposition. It is not a simple dissociation; but the decomposition should be preceded by a polymerisation, the condensed product immediately separating into carbonic acid and sub-oxides. The mechanism of this singular transition from this point obeys the same laws as the pyrogenous decompositions and polymerisations of the carbides of hydrogen.

But few experiments have been made from the quantitative point of view. Lowthian Bell has given a large number of determinations relative to the quantities of carbon deposited on known weights of metallic oxides at different temperatures; but he did not estimate the proportions of carbonic acid and of carbonic oxide which were formed.

It occurred to me that it would be interesting to take up this question again; from the theoretical point of view the reaction $2CO=CO_2+C$ comes under the heading of reversible phenomena; from the practical point of view it plays an important part in the working of gas producers. The decomposition of carbonic oxide in fact explains why it is impossible, above all at low temperatures, to obtain this gas without carbonic acid, which is the rule in poor commercial gas. Further, in the metallurgy of iron it would be useful to have numerical data on the decomposition of carbonic oxide in the presence of oxide of iron at different temperatures.

The experiments of Lowthian Bell relative to the decomposition of carbonic oxide in the presence of metallic oxides have shown that the most favourable temperature for the deposition of carbon is 400—450°. According to this *savant*, the difference of importance observed in the deposits of carbon with the different oxides of iron belongs probably to a difference of structure, itself due to the difference of temperature to which the ores have been calcined; further, the phenomenon of the deoxidation of the mineral and that of the deposit of carbon cannot commence at the same temperature. Lowthian Bell therefore thought that the formula for the reaction should be the following:—

$$Fe_xO_y+3CO=3C+Fe_xO_{y+z},\ x>y.$$

If the action of carbonic oxide on Fe_2O_3 is considered at several intervals we have a mixture of iron, carbon, and an unknown oxide Fe_xO_y, and a series of very complex reactions is produced among the bodies present. According to Lowthian Bell there would, in fact, be a tendency towards the following reactions:—

1. Action of CO on Fe_xO_y, giving CO_2 and a lower oxide of iron.

2. Action of this lower oxide of iron on CO, giving Fe_xO_y and a deposit of carbon.

3. Action of the carbon on Fe_xO_y, giving the metal, the lower oxide, and a mixture of CO and CO_2.

4. Action of metallic iron on CO, giving Fe_xO_y, or the lower oxide, and setting carbon free.

5. Action of CO_2 on the carbon, the metallic iron, and the lower oxide.

There would thus be different equilibria between all the reactions.

I now give the results of researches carried out on oxides of iron, nickel, and cobalt, at a temperature of 445°, which is easy to obtain. I have successively varied the quantities of the metallic oxides in the reaction, and the duration of contact between the metallic oxide and the carbonic oxide.

The carbonic oxide is obtained by the action of sulphuric acid on formate of soda; the gas produced containing 95 to 97 per cent of pure carbonic oxide is collected in Regnault gas-holders. Before entering into reaction it traverses a copper tube 25 c.m. in length, heated to redness, a flask of potash, and a U-tube containing fragments of potash. A control tube containing baryta water shows that the carbonic oxide is completely deprived of carbonic acid before reaching the sulphuric acid drying tubes.

The metallic oxides are used in a very finely divided state, pumice being used to give support (this pumice soaked with the nitrate is calcined at a red heat); they are contained in glass tubes of 15 m.m. internal diameter and 60 to 70 m.m. in length, drawn down to a point at each end. These tubes are placed in communication with the carbonic oxide. When the metallic oxides are completely reduced and there is a deposit of carbon (the gas should be passed for about an hour to effect this), the tube is closed and then heated for some time. At the end of the experiment the tube is taken from the sulphur bath, and the gases extracted by means of a mercury pump and analysed.

The gas must be very carefully extracted while the tube is still warm; there is, in fact, a risk of the formation of metallic compounds with carbon, which the oxide might possibly furnish (sub-carbonate of iron, nickel, and prob-

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TABLE I.

Quantities of metallic oxides.	Eight mins.		Forty mins.		Sixty-four mins.		Eighty mins		Three hours.		Six hours.		Seven hours.	
	CO_2.	CO.	CO_2.	CO.	CO_2.	CO.	CO_2	CO.	CO_2.	CO.	CO_2.	CO.	CO_2.	CO.
Oxide of iron 0·0673 grm. ..	30·2	69 8	57·4	42·6	—	—	87·0	13·0	94·8	5·2	100	—	—	—
,, 0·224 ,, ..	16·1	83 9	—	—	62 9	37·1	—	—	—	—	—	—	100	—
,, 0·222 ,, ..	2·9	97·1	—	—	36·6	63·4	—	—	—	—	52·3	47·7	—	—

TABLE II.

Quantities of metallic oxides.	Eight minutes.		Sixty minutes.		Two hours.		Four hrs. 15 mins.	
	CO_2.	CO.	CO_2.	CO.	CO_2.	CO_2.	CO_2.	CO.
Oxide of nickel 0·15 grm. ..	100	—	—	—	—	—	—	—
,, 0·05 ,, ..	90·9	9·1	100	—	—	—	—	—
,, 0·005 ,, ..	25·9	74·1	88·4	11·6	96 3	3·7	100	—
Oxide of cobalt 0·15 grm. ..	100	—	—	—	—	—	—	—
,, 0·05 ,, ..	89 7	10·3	100	—	—	—	—	—
,, 0·005 ,, ..	47·6	52·4	81·2	18·8	93 9	6·1	100	—

ably cobalt). I noticed this fact with some tubes containing oxide of nickel which had been closed in August, 1898, and were opened in the following October. The pieces of pumice contained in the tube, on being heated, gave rise to the formation of a metallic film, due to the decomposition of the sub-carbonate of nickel formed on cooling. The most favourable temperature for the formation of sub-carbonate of nickel is about 50°.

I. The experiments were carried out on quantities of metallic oxides varying in the proportion of 30 to 1; the time of heating varied from eight minutes to seven hours. The results obtained were as follows. (See Tables I. and II.).

These figures indicate the quantities per 100 of carbonic acid formed and of undecomposed carbonic oxide. Together these results show that the reaction of the decomposition of the carbonic oxide is a function of time, and that it also depends on the quantity of metallic oxide present. With the oxides of nickel and cobalt a much longer time is required than with oxide of iron to arrive at complete decomposition. In the third set of experiments, made with oxide of iron, after six hours heating the decomposition was not complete; but there is no doubt that after the lapse of a sufficiently long time a result would be obtained identical with the others.

II. In the above-mentioned experiments, both with the oxide of iron and the oxides of nickel and cobalt, the quantities of carbon deposited at the moment of closing the tubes was in the same proportion as the quantities of metallic oxides present. In a second series of experiments, I took wood-charcoal, calcined in a current of chlorine to remove what hydrogen it might contain; this carbon, in fragments about the size of a nut, was impregnated with a solution of nitrate of iron, nickel, or cobalt, and calcined. I then had to do with large quantities of carbon relative to the quantities of oxide present; with iron the proportion of carbon was 13 : 1; with nickel and cobalt, 9 : 1. The experiments were carried out in the same manner as the preceding ones and at the same temperature, viz., 445°. The results were as follows:—

TABLE III.

Quantities of metallic oxides.	Eight minutes.		Six hours.	
	CO_2.	CO.	CO_2.	CO.
Oxide of iron 0·244 grm. ..	33·3	66·7	84·1	15·9
,, 0·008 ,, ..	7·9	92·1	79·7	20·3
	Eight minutes.		Four hours fifteen mins.	
Oxide of nickel 0·244 grm. ..	64·0	36·0	99·1	0·9
,, 0·0158 ,, ..	25·3	92·1	65·4	34·6
Oxide of cobalt 0·417 ,, ..	96·4	3·6	98·8	1·2
,, 0·0139 ,, ..	17·4	82·6	84·4	15·6

The progress of the reaction is thus the same: we get total decomposition of carbonic oxide by sufficiently prolonging the heating. With the oxides of nickel and cobalt a shorter time is required than with oxide of iron to arrive at the same results. We would, however, remark in a general way that there is a slowing down of the phenomenon; and that, other things being equal, in this second series of experiments the decomposition of the carbonic oxide is effected much more slowly.—*Bull. Soc. Chim.*, Series 3, xxi., No. 6.

SOME PROPERTIES OF LIQUID AMMONIA.

By E. C. FRANKLIN and C. A. KRAUS.

THE authors have been led to undertake the study of the properties of liquid ammonia in considerable detail with the object of following out, to as great an extent as possible, the manifest close relation which exists between this solvent and water. Although it has long been recognised that many derivatives of water have their analogues in certain ammonia derivatives, still the intimate relation existing between the two liquids seems never to have been fully recognised.

Water occupies an essentially unique position among the well-known solvents. Its physical properties, such as its capacity as a general solvent for salts and its power of electrolytic dissociation, its low molecular elevation constant, its high boiling-point, and its heat of fusion, heat of volatilisation, critical temperature and critical pressure, specific heat, association constant and dielectric constant, with values so very much higher than the corresponding values for other substances, all tend to remove it far from other solvents, and to place it in a class by itself.

From the considerations submitted below it will be recognised that, of all known liquids, ammonia most closely approaches water in all those properties which give to water its conspicuous position among solvents. In its capacity as a general solvent for salts it is secondary to water, but superior to all other solvents. It closely approaches water in its power of dissociating electrolytes; some salts conduct electricity even better in ammonia solution than they do in aqueous solution. It plays a part in many compounds analogous to that occupied by water in salts containing water of crystallisation. Its heat of volatilisation and probably its association constant are higher than those of any other liquid with the one exception of water. For a substance of such simple composition its critical temperature and critical pressure, and even its boiling-point at atmospheric pressure, are remarkably high, as is still more conspicuously true of the corresponding constants in the case of water. Its specific heat is quite as great as that of water, while its molecular elevation constant is lower than that of any other substance for which measurements have yet been made.

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Ammonia differs from water in its inability to dissolve the sulphates and sulphites, the alkaline carbonates, phosphates, and oxalates, the hydroxides of the alkali and alkaline earth metals, and the facility with which it dissolves many organic substances, in which latter respect it reminds one of alcohol rather than of water. The liquid does not exhibit a maximum density (Faraday, "Watts's Dictionary," 2nd Ed., vol. i., p. 183) above the freezing-point, nor is the solid ammonia specifically lighter than the liquid at its freezing-point, as is true of solid and liquid water.

Electrolytic Conductivity of Ammonia Solutions.—Bleekerode (*Phil. Mag.*, 1878, [5], v., 384, and *Wied. Ann*, 1878, iii., 161), in a paper published in 1878, on the conductivities of the liquefied halogen acids, ammonia, and certain other compounds, makes the statement that liquid ammonia is a good conductor of electricity. There can be no question, however, that he misinterpreted his results. The conductivity he measured was undoubtedly due to a salt of sodium in solution. The passage of the current decomposed the salt, setting free metallic sodium, which, dissolving in the ammonia, gave to the solution the characteristic blue colour.

Divers, in 1873, observed that the concentrated solution of ammonium nitrate in liquid ammonia, formed by the deliquescence of the salt in an atmosphere of ammonia gas, is a good electrolytic conductor (*Proc. Roy. Soc.*, 1873, xxi., 109.

Led to the subject by the study of the similarity of properties, and of constitution of the compounds of salts with water of crystallisation to those compounds in which ammonia plays an analogous part, Cady (*Jour. Phys. Chem.*, 1897, i., 707) discovered that solutions of certain salts in liquid ammonia are conductors of electricity. He measured the conductivity of thirteen salts at moderate concentration, and found that they conduct electricity in ammonia solution at −38°, almost, if not quite, as well as they do in water solution at 18°. He also found that solutions of the alkali metals conduct electricity, and with much greater facility than do salt solutions. Moreover, he pointed out that these metallic solutions show no signs of polarisation at the electrodes.

The authors have extended the list of determinations of the conductivity of metallic salts, and have also made measurements of the conductivity of certain organic compounds, especially the aromatic nitro-compounds, which show themselves to be good conductors in solution in ammonia. The authors have also made measurements of the increase of molecular conductivity with dilution for a number of salts, and have, further, determined the conductivity of a number of solutions at temperatures varying from −79° up to and past the critical temperature of ammonia. The results of this work will be published in the near future.

Metathetic Reactions in Ammonia Solutions.—As in the case of aqueous solutions, electrical conductivity and facility of chemical reaction between substances in solution go hand in hand, so, because of the undoubtedly dissociated condition of salts dissolved in liquid ammonia, precipitates ought to be formed instantaneously when solutions containing ions which are capable of forming salts insoluble in ammonia are brought together. That ammonia solutions do exhibit such behaviour is shown by the results given in the preceding paper on "Metathetic Reactions between Certain Salts in Solution in Liquid Ammonia."

Ammonia of Crystallisation and Ammonia of Constitution.—The authors have up to the present added but one compound to the long list of substances formed by the direct addition of ammonia to many of the metallic salts. Leaving out of consideration at the present time the very great number of such compounds, it will be sufficient to mention the early observations of Divers (*loc. cit.*), who considers the ammonia in the liquid formed by the action of ammonia on ammonium nitrate to be entirely analogous in function to the water absorbed, for instance, by calcium chloride; to the ammonia addition-products described by Joannis (*Compt. Rend.*, 1891, cxii., 337), Jarry (*Ibid.*, 1897, cxxiv., 288 and 963; 1898, cxxvi., 1138), Bonnefoi (*Ibid.*, 1897, cxxiv., 771), formed by the action of liquid ammonia on the salts, and to the slaking phenomena attendant upon the action of liquid ammonia on certain halogen salts first described by Gore (*Proc. Roy. Soc.*, 1872, xx., 441), and also observed by the authors in their investigations on liquid ammonia as a solvent (*Amer. Chem. Journ.*, xx., 820).

Specific Heat of Ammonia.—The specific heat of liquid ammonia has been calculated from thermodynamic data by Zeuner, Ledoux, and Wood. It has also been made the subject of experimental investigation by Regnault, Von Strombeck (*Journ. Frank. Inst.*, 1890, cxxx., 467), Lüdeking and Starr (*Am. J. Sci.*, 1893, [3], xlv., 200), and Elleau and Ennis (*Journ. Frank. Inst.*, 1898, cxlv., 189). For the experimentally determined values, Von Strombeck found 1·22876 at 45°, Lüdeking and Starr 0·8857 at 40°, and Elleau and Ennis 1·021 at 10°. Calculated from Professor Wood's formulæ ("Thermodynamics," p. 325; *Trans. A. I. M. E.*, xii., 136, and x., 645.

*Boiling-point of Ammonia.**—While the boiling-point of ammonia is much below that of water, still it is high when compared with the boiling-points of other simple compounds of elements with low atomic weights. The boiling-points of hydrogen sulphide, hydrogen selenide, the halogen acids, methane, ethylene, acetylene, phosphine, and even arsine, stibine, and hydrogen telluride, are all below, and some of them far below, the boiling-point of ammonia. As is the boiling-point of water, so is the boiling-point of ammonia—although to a less extent—abnormally high.

Heat of Fusion.—No determinations of the heat of fusion of solid ammonia have yet been made.

Heat of Volatilisation of Ammonia.—With the exception of some preliminary measurements by the authors, no direct determinations of the heat of volatilisation of ammonia at its boiling-point at atmospheric pressure have yet been made. Regnault's value (Landolt and Börnstein, "Physikalisch-chemische Tabellen") of 294·21 is the result of measurements made at 7·8°. Von Strombeck (*loc. cit.*, p. 472) obtained 292·4 as the result of measurements made at 14° to 18°. As preliminary results the authors have obtained 326 to 332 as the heat of volatilisation of ammonia at its boiling-point. A description of the method by which these measurements were made, together with the final values, will be published in a later paper.

The heat of volatilisation of ammonia at any required temperature may also be calculated from thermodynamic formulæ. From a formula used by engineers in calculating the capacities of refrigerating-plants, $h_e = 300 - 0{\cdot}8t$ (Peabody, "Thermodynamics," p. 459), the value for the heat of volatilisation of ammonia at −38° is calculated to be 330 calories.

Another formula given by Professor Wood ("Thermodynamics," p. 332), $h_e = 555{\cdot}5 - 0{\cdot}613T - 0{\cdot}000219T$, in which English heat units and Fahrenheit temperatures are to be understood, if used for calculating the heat of volatilisation of ammonia, gives a value of 321 cals. at −38° C.

The heat of volatilisation of a liquid may also be calculated by means of the law of Trouton (*Phil. Mag.*, 1888, [5], xviii., 54), according to which the molecular heats of volatilisation of closely related substances are directly proportional to their absolute boiling-points. In the expression for Trouton's law $\lambda M/T = k$, in which λ is the heat of volatilisation, M the molecular weight, and T the absolute boiling-point, the values of k, in the case of water, methyl alcohol, ethyl alcohol, and amyl alcohol

* Regnault gives 38·5°; Loir and Drion 35·7°; and Bunsen 33·7° as the boiling-point of ammonia. "Watts's Dict. Chem." 2nd Ed., vol. i., p. 183; "Supplement," vol. vi., p. 102. Joannis gives the boiling-point at 38·2°, *Compt. Rend.*, 1893, cxv., 820.

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are respectively 25·9, 25·7, 26·3, and 26·2. If we are justified in assuming that ammonia is closely related to water, then by substituting the values, $k = 25·9$, $T = 235$, and $M = 17$, in the formula $\lambda = kT/M$, the latent heat of volatilisation of ammonia is calculated to be 358 cals.

These values, while not in as good accord as might be wished, still agree in showing that the heat of volatilisation of liquid ammonia, of all known liquids, is second only to water.

Molecular Elevation Constant of Ammonia.,— Other than by direct experimental determination, the molecular elevation constant of a liquid may be calculated by means of the formula of van 't Hoff, provided the heat of volatilisation and the boiling-point of the liquid are known. Several approximate values for the heat of volatilisation of ammonia are given above, which by substitution in the formula, $k = 0·02T^2/\lambda$, yield the values given below for the molecular elevation. Values for the molecular elevation of the boiling-point, experimentally determined for a number of substances (*Amer. Chem. Journ.*, xx., 836) are also included in the table.

	he.	*k.*
Peabody's formula ..	329	3·35
Wood's ,, ..	321	3·44
Trouton's ,, ..	358	3·09
He direct	329	3·36
Water		3·4
Ethyl alcohol.. ..		3·4
Propyl ,, ...		3·4 to 2·7
Pyridine		3·3 to 1·8
Aniline		3·9 to 3·1
Potassium iodide ..		3·2 to 5·9

Certainly the molecular elevation of the boiling-point of ammonia is smaller than that of any other solvent for which measurements have yet been made.

The Dielectric Constant of Ammonia.—This constant has recently been measured by Dr. H. M. Goodwin (a paper read before Sec. B, American Association for the Advancement of Science, 1898), of the Massachusetts Institute of Technology, who finds a value of about 20. These measurements, if Nernst's hypothesis holds true, show that the dissociation of salts in liquid ammonia may not be as great as we had supposed.

Molecular Association of Ammonia.—Some indication of the degree of association of a liquid may be arrived at by the application of the methods given by J. Traube in a recent paper (*Ber. d. Chem. Ges.*, 1897, xxx., 265).

For liquid ammonia we have calculated the values, $190 - _{\infty}$, 23·9, and 0·00079, for—

$$\varkappa_2 \frac{M\lambda}{T} \text{ and } \frac{MT' - T}{m \rho T}$$

especively (*loc. cit.*, p. 273), results which place liquid ammonia among the associated liquids along with water and the alcohols.

If 55·90, the approximate molecular heat of volatilisation of ammonia, be substituted in place of an incorrect value used in a table recently published by Vaubel (*Jour. Prakt. Chem.*, 1898, [5], lvii., 351), then the association constant of liquid ammonia approaches that of water and excels that of the alcohols instead of indicating ammonia to be a non-associated liquid.—*American Chemical Journal*, xxi., No. 1.

Some Derivatives of Disymmetric Tetramethyldiamidodiphenylethane. — A. Trillat. — The base obtained by condensing acetic aldehyde with dimethylamine shows a close analogy to the derived base of methane. It differs from it, however, essentially in one particular, that it is unable to form colouring-matters. —*Comptes Rendus*, No. 23, June 5, 1899.

PROCEEDINGS OF SOCIETIES.

PHYSICAL SOCIETY.

Ordinary Meeting, June 23rd, 1899.

Mr. T. H Blakesley, Vice-President, in the Chair.

A paper "*On the Magnetic Hysteresis of Cobalt*," by Prof. Fleming, Mr. A. W. Ashton, and Mr. H. J. Tomlinson, was read by Mr. Ashton.

A rectangular sectioned circular ring of cobalt was insulated with silk tape, and wound over with four secondary coils put on at quadrantal positions. Over these secondary coils six primary coils were placed, and the ring was submitted to a complete set of magnetic tests with a ballistic galvanometer.

From these observations various curves have been plotted, and the results have been compared with a similar set of readings taken on a cast-iron ring. A chemical analysis of the cobalt showed that it contained about 1 per cent of iron and 1 per cent of nickel. The authors conclude that, although in general form the magnetisation curve for cobalt resembles that of cast-iron, its hysteresis exponent is similar to that of annealed soft iron. The absolute hysteresis values corresponding to various maximum flux densities are, however, not very different from those of a typical variety of cast-iron.

Prof. Everett referred to the fact that the sample of cobalt contained about 1 per cent of iron, and said that it would be interesting to know how cobalt free from iron would behave.

The Chairman said that the hysteresis curves obtained from the step by step method could not be applied to dynamos, because the time taken to perform the cycle altered the shape of the curve. He would like to see the curves for cobalt determined in cases where the cycles were quickly executed.

A "Discussion on Physical Tables" was commenced by Mr. J. Lupton.

Mr. Lupton briefly reviewed some of the difficulties met with in compiling Physical Tables and in keeping them up to date. He divided them into four classes according to their objects, and criticised several well-known books of constants. He pointed out the danger of leaving out apparently obvious figures, and referred to the necessity for accurate proof reading.

Prof. Everett said that, in his work, he had aimed at giving an idea of the meanings of various numbers rather than stating them with great accuracy. He drew attention to the difficulty of condensing large series of numbers into a clear and concise table.

Mr. Watson said that it was important that the units in which numbers were expressed should be stated at the head of each table.

The Chairman having pointed out one or two small points to be attended to in the compilation of tables, the Society adjourned until next October.

Electrolytic Estimation of Cadmium.—E. Rimbach. —The best means for effecting this separation is to use about 150 to 200 c.c. of the dilute solution, add an excess of pure cyanide of potassium, and electrolyse with a current of 0·02 to 0·04 ampère and 3·0 to 3·3 volts. The electrolysis must be kept up for twelve hours, after which the cathode is washed, dried, and weighed. This method is especially suitable for the analysis of alloys containing aluminium, cadmium, and tin, with small quantities of copper. The alloy is dissolved in nitric acid, evaporated in the presence of an excess of hydrochloric acid, and the solution of chlorides electrolysed. By this process we are also enabled to separate cadmium from magnesium, if this latter metal is not present in too great proportion. In such a case an excess of chloride of ammonium must be added to the electrolyte to prevent the precipitation of the magnesium.—*Zeit. Anal. Chem.*, xxxvii., [5], p. 284.

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CHEMICAL NOTICES FROM FOREIGN SOURCES.

Note.—All degrees of temperature are Centigrade unless otherwise expressed.

Comptes Rendus Hebdomadaires des Séances, de l'Académie des Sciences. Vol. cxxviii., No. 22, May 29, 1899.

Estimation of Hydrogen Phosphide in Gaseous Mixtures.—A. Joannis.—The author's experiments show that sulphate of copper can only be employed to estimate phosphoretted hydrogen contained in gaseous mixtures in the absence of gases which are absorbed by copper salts. In the latter case, only a quantity of copper sulphate sufficient for the reaction must be used—two molecules of sulphate to one of phosphide. For example, 1 c.c. of the saturated solution for 10 c.c. of the gas.

Separation and Estimation of Traces of Chlorine in presence of a very Large Excess of Bromine.—A. Baubigny.—In several recent papers, a method of estimating small traces of chlorine by the action of bromine on chlorides has been described. The author's researches show that in dilute solution, relatively poor in chlorides, the salts appear to undergo no alteration, in spite of the presence of a large excess of free bromine. By his modification of this method minute traces of chlorine are able to be detected in bromides.

Properties of some Mixed Halogen Salts of Lead.—V. Thomas.—By dissolving lead iodide in a saturated hot solution of lead bromide, greenish yellow needles of bromiodide are deposited; the first crop having the formula $3PbBr_2PbI_2$. Analysis of the resulting product shows gradually less and less of the iodide. At a low temperature the crystals are formed of pure lead bromide. If, instead of separating the first crops of crystals by filtration, they are left to cool in the solution, the whole is transformed into bromiodide. On heating the solution the crystals dissolve and decompose. These results can be easily explained if the fact of the dissociation of the mixed salts is admitted.

Quantitative Separation of Cerium.—G. Wyrouboff and A. Verneuil.—The great difficulty of separating quantitatively any single one of the rare earth group is due to two properties common to these earths: their polymerisation and their faculty for forming exceedingly stable compounds among themselves. To estimate the cerium present in presence of other rare earths, the nitric acid solution of their oxides is precipitated by ammonia and peroxide of hydrogen. This is evaporated on a water-bath and heated for a few moments until the NH_4NO_3 begins to volatilise. The whole is then dissolved again in HNO_3 and evaporated to a syrupy state, but not further, dissolved in boiling water, and a slight quantity of $(NH_4)_2SO_4$ added. The precipitate formed is filtered, washed, and heated to a white heat. If the operation has been successful, the product should contain 90 per cent of the total cerium in a perfectly pure state. The filtrate is then added to 0·05 gr. of ammonium persulphate and 1 c.c. of 50 per cent acetate of soda solution. The whole is boiled until the liquid becomes clear and well separated from the precipitate, which latter is filtered, washed, and strongly heated. This precipitate should consist of the remainder of the cerium of a pale yellow colour.

Mixed Compounds of Phenylhydrazine and another Organic Base with Metallic Salts.—J. Moitessier.—Certain combinations of metallic salts with phenylhydrazine can be made to unite with further molecules of this base, giving compounds very rich in phenylhydrazine. In the same manner they can be made to unite with other organic bases (aniline, naphthylamine, &c.), giving mixed compounds. These latter compounds can be also prepared by the simultaneous action of phenylhydrazine and another organic base on the metallic salts. The author prepared the following compounds by this method:—

Aniline phenylhydrazinic iodide of zinc,—

$$ZnI_2.C_6H_5.NH_2.2C_6H_5.N_2H_3;$$

aniline phenylhydrazinic bromide of zinc,—

$$3ZnBr_2.5C_6H_5.NH_2.2C_6H_5.N_2H_3;$$

aniline phenylhydrazinic sulphate of nickel,—

$$NiSO_4.C_6H_5.NH_2.2C_6H_5.N_2H_3+2H_2O;$$

aniline phenylhydrazinic nitrate of cadmium,—

$$2N_2O_6Cd.3C_6H_5.NH_2.5C_6H_5.N_2H_3;$$

α-naphthylamine phenylhydrazinic iodide of zinc,—

$$ZnI_2.C_{10}H_7NH_2.2C_6H_5.N_2H_3;$$

β-naphthylamine phenylhydrazinic iodide of zinc,—

$$3ZnI_2.2C_{10}H_7.NH_2.4C_6H_5.N_2H_3.$$

Oxymethylenic Derivatives of Cyanacetic Ether.—E. Grégoire de Bollemont.—The author has prepared a series of compounds from the sodium salt, which is prepared by the action of amyl formate on dry cyanacetic ether at 100°. From this are prepared the barium salt,—

and the silver salt,—

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Action of Bibromide of Acetylene on Pyrocatechin in the presence of Alkalis.—Ch. Moureu.—One molecule of bi-bromide of acetylene, one molecule of pyrocatechin, and two molecules of alkali are added together. A reaction takes place, but not the one expected; there is no action in the cold, but it occurs with violence—and sometimes with explosive force—under the influence of heat. Whether the alkali is in aqueous or alcoholic solution, dilute or concentrated, bromised acetylene gas, $CH{\equiv}CBr$, is formed rapidly by heating; this gas ignites spontaneously in the air with the production of a thick smoke. Di-soda or di-potash pyrocatechin reacts on bromide of acetylene, with the elimination of hydrobromic acid, in the same manner as with free alkali, and ethenic pyrocatechin is not formed.

Glyoxal Dipyrocatechin.—Ch. Moureu.—One molecule of tetrabromide of acetylene was gradually added to a mixture of two molecules of pyrocatechin, four molecules of potash, and water equal to about one quarter the weight of the potash. This was shaken continuously and kept at a temperature of about 60°. The reaction is very lively, and gas is given off abundantly. Finally, the whole is heated in a flask fitted with a vertical condenser in an oil-bath for four hours. The cooled mass is then treated with an excess of potash or soda-lye and submitted to the action of a current of steam. The various phenolic compounds remain in the alkaline solution and a neutral oily substance is gradually carried over, and condenses in the form of white masses completely insoluble in water. The product crystallises in alcohol in thin light leaflets, melting at 88—89° and having the formula $C_{14}H_{10}O_4$. This new compound appears to be a normal regular condensation product of glyoxal and of pyrocatechin, for which we propose the name glyoxal-dipyrocatechin. After heating this new body with dilute sulphuric acid for four hours in the same flask, pyrocatechin is found in the water of hydrolysis, but no glyoxal. It is also shown, however surprising it may be, that glyoxal-dipyrocatechin, glyoxalic diacetal of pyro-

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catechin, and consequently the aldehydic derivatives, furnish by simple hydratation a compound at the same time acid and phenolic, viz., orthoxyphenoxyacetic acid.

On Glyoxal-monopyrocatechin Aldehyde.—Ch. Moureu.—According to the preceding paper, glyoxal-monopyrocatechin aldehyde, $C_6H_4<^{(1)\,O}_{(2)\,O}>CH-CHO$, should necessarily constitute the first intermediate product of the hydrolysis of glyoxal-dipyrocatechin, $C_6H_4<^{O\ (1)}_{O\ (2)}>CH-CH<^{O\ (1)}_{O\ (2)}>C_6H_4$. From this it follows that this aldehyde, when hydrolysed directly, should produce orthoxyphenoxyacetic acid, as does glyoxal-dipyrocatechin itself. The author then goes on to show that such is really the case.

On Orthoxyphenoxyacetic Acid, and on Phene-orthodioxyacetic Acid.—Ch. Moureu.—This note sums up a certain number of facts which have been observed in the course of the work described in the two previous papers, but which are not in immediate relation with this work. (1) Orthoxyphenoxyacetic acid is not a phenolic acid properly speaking, the carboxyl not being directly linked to the aromatic nucleus; the substance is in reality a substituted acetic acid. Its ethylic ether is easily obtained by heating with a reflux condenser equal molecules of monochloracetate of ethyl and mono-soda pyrocatechin in alcoholic solution. (2) At the same time as the above acid is formed, there is also another one arising from the condensation of monochloroacetic acid with pyrocatechin. The mother-liquors from this preparation slowly deposit a white powder, forming, after crystallisation, fine needles melting at 172—174°. This compound is phene-ortho-dioxyacetic acid, $C_6H_4<^{O-CH_2-CO_2H\ (1)}_{O-CH_2-CO_2H\ (2)}$.

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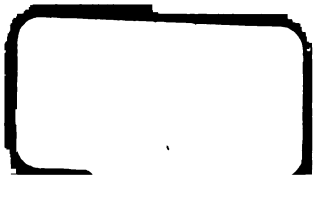

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